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(54) CARBON FIBER, AND PRODUCTION OF PRECURSOR FOR CARBON FIBER

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain carbon fibers, lightweight, high in tensile strength, excellent in adhesion to resins and cost performance, and useful for composite materials or the like, by keeping their surface area ratio in a specific range.

SOLUTION: This fiber has a surface area ratio of 1.02 to 1.09; tensile strength of preferably 5.5 GP a or more; interlaminar shear strength of 90 MPa or more; Si/C atomic ratio of 1 or less at a depth of 50 nm from the fiber surface, determined by SIMS; Si/C atomic ratio of 0.01 or less on the fiber surface, determined by ESCA; and spreadability index of 20 to 40. This carbon fiber can be obtained by firing a precursor comprising an acrylic-based fiber, having a hook drop length of 20 cm or less and obtained by drawing, to 4 times or less, the filament yarn spun by wet spinning in such a state that the swelling degree is in 50-300 wt.%, and drying and densifying the yarn.

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[Claims for the Patent]

[Claim 1]

A carbon fiber characterized by having a surface area ratio of 1.02 to 1.09.

[Claim 2]

The carbon fiber according to claim 1, characterized by having a tensile strength of 5.5 Gpa or more and an interlaminar shear strength of 90 MPa or more.

[Claim 3]

The carbon fiber according to claim 1 or 2, characterized in that the precursor thereof is an acrylic fiber obtained by a wet spinning method.

[Claim 4]

The carbon fiber according to any one of claims 1 to 3, wherein the number-of-atoms ratio between Si and C (Si/C), obtained by SIMS, at the depth of 50 nm from the surface of the fiber is 1 or less.

[Claim 5]

The carbon fiber according to any one of claims 1 to 4, wherein the number-of-atoms ratio between Si and C (Si/C), obtained by ESCA, on the surface of the fiber is 0.01 or less.

[Claim 6]

The carbon fiber according to any one of claims 1 to 5, wherein the spreadability index thereof is 20 to 40.

[Claim 7]

The carbon fiber according to any one of claims 1 to 6, obtained by firing a precursor having a hook drop length of 20 cm or less.

[Claim 8]

A production method of a precursor for carbon fiber, characterized in that the precursor is obtained, in a wet spinning method, by spinning a filament, drawing at a magnification of 4 or less the filament with a swelling degree of 50 to 300% by weight, and then drying and densifying the filament.

[Claim 9]

A production method of a precursor for carbon fiber, characterized in that the precursor is obtained, in a wet spinning method, by spinning a filament, drawing the filament while maintaining the swelling degree of the filament at 225% by weight or less, and then drying and densifying the filament.

[Claim 10]

A carbon fiber-reinforced composite material excellent in strength properties which is obtained from the carbon fiber according to any one of claims 1 to 7.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a carbon fiber in which the strength and the adhesiveness to resin are compatible, and which is also excellent in cost performance, and relates to a production method of a precursor for carbon fiber.

[0002]

[Conventional Art]

Carbon fiber is superior to other fibers in specific strength and specific elastic modulus, and hence is widely used in industry as a reinforcing material in production of composite materials with a resin, taking advantage of the lightweightness and excellent mechanical properties of the carbon fiber. In recent years, the superiority of carbon fiber-reinforced composite materials has been increasingly elevated, and particularly in applications to sports and aerospace, further enhancement of the performances of carbon fiber and carbon fiber-reinforced materials has been demanded.

[0003]

Carbon fiber breakage occurs, in most cases, starting from microdefects (hereinafter, abbreviated as surface defects) present on the surface thereof. Accordingly, achievement of high performance of carbon fiber requires to make consideration so that generation of such surface defects may be suppressed as completely as possible in the production process thereof. As methods for removing

surface defects after the generation thereof, JP-A-58-214527 and JP-A-61-225330 have proposed methods in which carbon fiber is subjected to a post-treatment such as a vapor phase treatment, a liquid phase treatment or an electrolytic oxidation treatment to subject the surface layer of carbon fiber to an etching treatment, and thus the surface defects are compulsorily removed.

[0004]

However, according to these methods, although the strength of the carbon fiber thus obtained is improved, the operations and process involved therein become extremely cumbersome, and the production cost is drastically increased, and hence it has been difficult to adopt these methods as practical production techniques. As for carbon fiber, further reduction of price thereof as well as enhancement of the performance thereof is highly demanded, and accordingly, as matters now stand, carbon fibers with high cost performance are exclusively accepted in the market.

[0005]

When a precursor for carbon fiber is produced by a wet spinning method, in many cases, breakage starts from the irregularities of the fibril structure characteristically generated in the wet spinning method and the strength is impaired. Accordingly, JP-A-62-141124 proposes a method in which a dry-wet spinning method is adopted to decrease the coagulation tension and such irregularities are thereby decreased.

[0006]

However, according to this method, although the strength of the obtained carbon fiber is improved, the reduced irregularities on the surface of the fiber lead to decrease of the adhesiveness to resin, and the characteristics of carbon fiber as reinforcing fiber sometimes may not be fully attained.

[0007]

On the other hand, as applications related to energy, high-performance flywheels are being developed for leveling of electric power demand and for uninterruptible power sources, and compressed natural (CNG) gas automobiles are being developed for the purpose of reducing carbon dioxide exhaust emission; in these developments, it has been planned to adopt carbon fiber as raw materials for rotors and gas storage tanks.

[0008]

These applications mainly take advantage of the excellent tensile strength properties of carbon fiber; high adhesiveness to resin as well as the tensile strength has been demanded, as for rotors undergoing radial dilation and distortion due to centrifugal force while rotating at high speeds, for the purpose of resisting to the force to tear off fiber from resin, and as for gas storage tanks, for the purpose of preventing the deterioration of the properties subsequent to fatigue caused by repeating gas charge and discharge and preventing the degradation of the residual strength subsequent to collision of objects.

[0009]

With the above described circumstances as background, there have been strongly demanded carbon fiber ensuring high adhesiveness to resin while maintaining high tensile strength and a method for obtaining such carbon fiber at low price and easily.

[0010]

[Problems to be Solved by the Invention]

Objects of the present invention are to provide a carbon fiber in which the tensile strength and the adhesiveness to resin, usually with a trade-off relation therebetween, are compatible with each other at a high level, and which is also excellent in cost performance, to provide a production method of a precursor for carbon fiber, and furthermore, to produce a carbon fiber-reinforced composite material excellent in strength properties by using such carbon fiber.

[0011]

[Means for Solving the Problems]

For the purpose of solving the above described problems, a carbon fiber of the present invention has such a constitution that the carbon fiber has a surface area ratio of 1.02 to 1.09.

[0012]

A production method of a precursor for carbon fiber of the present invention has any one of the following constitutions for the purpose of solving the above described

problems.   Specifically, the production method of a precursor for carbon fiber of the present invention is a production method of a precursor for carbon fiber, characterized in that the precursor is obtained, in a wet spinning method, by spinning a filament, drawing at a magnification of 4 or less the filament with a swelling degree of 50 to 300% by weight, and then drying and densifying the filament, or a production method of a precursor for carbon fiber, characterized in that the precursor is obtained, in a wet spinning method, by spinning a filament, drawing a filament after the filament has been spun while maintaining the swelling degree of the filament at 225% by weight or less, and then drying and densifying the filament.

[0013]

[Embodiments of the Invention]

The inventors have achieved the present invention by finding that the strength properties (hereinafter, simply abbreviated as strength) typified by the 0° tensile strength and the adhesiveness to resin (hereinafter, simply abbreviated as resin adhesiveness) typified by the interlaminar shear strength can be made compatible with each other by focusing attention on and appropriately controlling the surface configuration of carbon fiber although the strength and the resin adhesiveness are usually conflicting with each other.

[0014]

The carbon fiber of the present invention has a surface configuration intermediate between such a carbon fiber having an extremely smooth surface that is obtained by a dry-wet spinning method and such a carbon fiber having a surface abundant in irregularities that is obtained by a wet spinning method.   In other words, the carbon fiber of the present invention has a high performance that has at the same time a feature of the former to have a high strength and a feature of the latter to have a high resin adhesiveness.   Hereinafter, detailed description will be made on the present invention.

[0015]

The carbon fiber of the present invention is characterized in that the surface area ratio thereof is 1.02 to 1.09.   Conventionally, the surface area ratio of a carbon fiber

that is said to have a smooth surface usually falls within a range from 1 or more and less than 1.02, and such a carbon fiber is excellent in strength but is inferior in resin adhesiveness. On the other hand, the surface area ratio of a carbon fiber that is said to have a surface abundant in irregularities usually exceeds 1.09, and such a carbon fiber is excellent in resin adhesiveness but inferior in strength. Accordingly, the inventors have made an intense research, and consequently have found that such a carbon fiber that has a surface area ratio falling within a range from 1.02 to 1.09 makes the strength and the resin adhesiveness compatible with each other at a high level. A surface area ratio falling within a range from 1.025 to 1.08 leads to a satisfactory result with respect to the compatibility between the strength and the resin adhesiveness. From such a viewpoint, the surface area ratio is desired to be more preferably 1.03 to 1.07, and furthermore preferably 1.035 to 1.06.

[0016]

In addition to the surface area ratio, as an index for quantification of the surface configuration of a carbon fiber, the root-mean-square roughness Rq of the three-dimensional roughness can be adopted. According to this index, for the compatibility between the strength and the resin adhesiveness, Rq is desired to be 10 to 24 nm, preferably 13 to 23 nm, and more preferably 16 to 22 nm.

[0017]

The tensile strength of the carbon fiber according to the present invention is desired to be, for the purpose of enhancing the performance of a carbon fiber-reinforced composite material (hereinafter, simply abbreviated as composite material), preferably 5.5 GPa or more, more preferably 5.7 GPa or more, furthermore preferably 6 GPa or more, and particularly preferably 6.5 GPa or more. A tensile strength of approximately 10 GPa is frequently sufficient to attain the advantageous effects of the present invention. For the purpose of enhancing the properties of a composite material, the ILSS of the carbon fiber of the present invention is preferably 90 MPa or more, more preferably 92 MPa or more, furthermore preferably 94 MPa or more, and particularly preferably 96 MPa or more. An ILSS value of approximately 120 MPa is frequently sufficient to attain the advantageous effects of the present invention.

[0018]

The carbon fiber according to the present invention may be derived from any of an acrylic origin, a pitch-based origin and a rayon-based origin, and is particularly a carbon fiber obtained by firing an acrylic precursor (hereinafter, simply abbreviated as precursor) for carbon fiber that has been obtained by spinning by a preferable method and under preferable conditions to be described later. As the spinning method, a wet spinning method is preferable, but a dry-wet spinning method or a dry spinning method may also be adopted. The firing as referred to in the present invention means a series of treatments in which a precursor obtained in a yarn-making step is successively subjected to a flame retarding step, a preliminary carbonizing step and a carbonizing step to yield a carbon fiber as a final product. Hereinafter, with reference to an example in which a precursor is produced by a wet spinning method, description will be made on a production method of the carbon fiber of the present invention.

[0019]

As raw material for a precursor, preferably used is a polymer that includes 85% by weight or more of acrylonitrile and 15% by weight or less of a polymerizable unsaturated monomer capable of copolymerizing with acrylonitrile. Examples of the polymerizable unsaturated monomer may include: acrylic acid, methacrylic acid, itaconic acid, and the alkali metal salts of these; acrylic acid, methacrylic acid, itaconic acid, and the ammonium salts of these; acrylic acid, methacrylic acid, itaconic acid, and the alkyl esters of these; acrylamide, methacrylamide and the derivatives of these; allylsulfonic acid, methallylsulfonic acid and the salts; and alkyl esters.

[0020]

For the purpose of promoting the flame retardation reaction, it is preferable that the above mentioned polymerizable unsaturated monomer is copolymerized with an unsaturated carboxylic acid or the like. The copolymerization amount, relative to the whole polymer, is desired to be 0.1 to 10% by weight, preferably 0.3 to 5% by weight, and more preferably 0.5 to 3% by weight. Specific examples of the unsaturated carboxylic acid may include acrylic acid, methacrylic acid, itaconic acid, crotonic acid,

citraconic acid, ethacrylic acid, maleic acid and mesaconic acid; preferred among these are acrylic acid, methacrylic acid and itaconic acid.

[0021]

For the purpose of improving the strength of the carbon fiber to be obtained as much as possible, it is desired that the above mentioned polymerizable unsaturated monomer is copolymerized with one or more selected from alkyl esters of unsaturated carboxylic acids and vinyl acetate. The copolymerization amount thereof, relative to the whole polymer, is desired to be 0.1 to 10% by weight, preferably 0.3 to 5% by weight and more preferably 0.5 to 3% by weight. Specific examples of the alkyl esters of unsaturated carboxylic acids may include methyl acrylate, methyl methacrylate, propyl methacrylate, butyl methacrylate, isobutyl methacrylate and secondary butyl methacrylate; preferred among these are the propyl, butyl, isobutyl and secondary butyl esters of acrylic acid and methacrylic acid.

[0022]

As the polymerization method for obtaining a polymer, the suspension polymerization method, the solution polymerization method or the emulsion polymerization method can be adopted. The polymerization degree of the polymer, in terms of the limiting viscosity (hereinafter, abbreviated as [η]) standard, is desired to be 1 or more, preferably 1.25 or more and more preferably 1.5 or more. It is to be noted that [η] is preferably set at 5 or less from the viewpoint of the spinning stability.

[0023]

A polymer solution prepared by dissolving such a polymer in a solvent is used as a spinning solution. As the solvent to be used for the polymer solution, there can be used an organic or an inorganic solvent. An organic solvent is preferable when there is adopted the wet spinning method in which the spinning solution is directly extruded for spinning into a coagulation bath through a spinneret. Specific examples of such an organic solvent may include dimethylsulfoxide, dimethylformamide and dimethylacetamide. When an inorganic solvent such as nitric acid, or a concentrated aqueous solution of an inorganic salt such as sodium rhodanate or zinc chloride is used, sometimes carbon fiber having a desired surface configuration cannot be obtained.

[0024]

After extrusion for spinning into the coagulation bath, the filament may be directly drawn, without washing with water, in a drawing bath, or may be drawn in a drawing bath after washing with water to remove the solvent. Such a drawing bath is usually formed with heated water regulated at temperatures of from 50 to 98°C, and the concentration of the above mentioned solvent is set to fall within a range from 0% by weight to the concentration of the solvent in the coagulation bath.

[0025]

In the present invention, it is the yarn-making step for producing the precursor, in particular, the drawing conditions for drawing the filament in the swollen state before drying and densifying that most significantly affects the surface configuration of the carbon fiber to be obtained. Accordingly, it is necessary to pay special attention to the drawing conditions.

[0026]

When the drawing magnification of the filament is too high in a swollen state in the bath before drying and densifying, there is a tendency that the irregularities on the filament surface develop excessively. Accordingly, for the purpose of obtaining a carbon fiber having a targeted appropriate surface configuration, it is necessary to carry out the drawing of the filament at a magnification of 4 or less under a condition of a swelling degree of the filament of 50 to 300% by weight before drying and densifying. For the purpose of obtaining a carbon fiber having a higher strength, such a drawing magnification is desired to be preferably 3 or less, more preferably 2.5 or less and furthermore preferably 2 or less.

[0027]

When such a drawing magnification is not at least approximately 1.1, the drawing property over the whole production step of the precursor cannot be ensured as the case may be.

[0028]

Conventionally, the decrease of such a drawing magnification leads to the decrease of the productivity and the increase of the production cost, it is difficult to

adopt the condition to decrease the drawing magnification. However, as will be described later, by appropriately regulating the drawing magnification after drying and densifying, the drawing property over the whole production step of the precursor is not lowered unexpectedly, and there can be obtained a carbon fiber having high performance without decreasing the productivity and increasing the production cost.
[0029]

When the drawing magnification of a filament in the drawing bath is relatively high, there is identified a region in which the swelling degree of the filament is increased, and it has been revealed that the irregularities of the filament surface occur abundantly in such a region, and drawing of the filament in such a state leads to remarkable development of the surface irregularities in the precursor and the carbon fiber. Accordingly, for the purpose of obtaining a carbon fiber having a desired appropriate surface configuration, it is necessary that the swelling degree of the filament in the drawing bath be maintained at 225% or less by weight when drawing is carried out, and the development of such surface irregularities be suppressed. The swelling degree of such a filament is preferably 215% by weight or less and more preferably 205% by weight or less. It is to be noted that, as matters now stand, it is difficult to make the swelling degree of a filament less than 50% by weight without applying a particular drying operation such as heating due to contact with a hot roller.
[0030]

When the temperature of the drawing bath is relatively high, the bonding between monofilaments tends to occur due to thermocompression bonding due to the entrance roller, and hence the entrance roller is desired to be installed outside the drawing bath. For the purpose of removing weak adhesion between monofilaments, it is desired to carry out the drawing while vibrating a filament bundle with a vibrating guide provided in the drawing bath. The vibrational frequency and the amplitude of such vibration are desired to be 5 to 100 Hz and 0.1 to 10 mm, respectively.
[0031]

The precursor according to the present invention has a smoother surface than that of a precursor obtained by a conventional wet spinning method, and tends to

undergo adhesion between single fibers at the time of drying and densifying or in the firing step; accordingly, it is desired to impart a silicone oiling agent to the filaments before drying and densifying. In this case, the silicone oiling agent is preferably imparted in a form of emulsion. Inclusion of an alkylene oxide-modified silicone in the silicone oiling agent is preferable from the viewpoint of enhancing the emulsion stability. Preferred as the alkylene oxide-modified silicone are an ethylene oxide-modified silicone, a propylene oxide-modified silicone and a silicone modified with these two alkylene oxides. The modification with an alkylene oxide imparts an appropriate hydrophilicity and hence the self-emulsifiability to the silicone oiling agent, and consequently, the silicone oiling agent can be made to have a function similar to that of a surfactant.

[0032]

Such treatments as described above conceivably create desirable properties in the silicone oiling agent such as the stability in water and the uniform adhesion onto the filament surface. The modification amount of a silicone with an alkylene oxide is desired to be 10 to 80% by weight and preferably 20 to 70% by weight; the modification amount less than 10% by weight sometimes leads to an insufficient self-emulsifiability, and the modification amount exceeding 80% by weight sometimes leads to degradation of the heat resistance.

[0033]

The number of the alkylene oxide units (repeating units) is preferably 25 or less from the viewpoint of ensuring the heat resistance of the silicone oiling agent. The larger is the molecular weight of a silicone, namely, the larger is the dynamic viscosity, the more improved is the heat resistance, and accordingly desired is a silicone having a dynamic viscosity at 25°C of 100 cSt or more, preferably 200 cSt or more and more preferably 300 cSt or more. It is to be noted that a silicone having a dynamic viscosity exceeding 10000 cSt is sometimes hardly dispersed in water.

[0034]

In addition to the alkylene oxide-modified silicone, an amino-modified silicone and/or an epoxy-modified silicone can be combined.

[0035]

The amino-modified silicone may be either a monoamine type or a polyamine type. The amino group may be introduced into a side chain or at a molecular chain terminal. In a modification exclusively carried out at a molecular chain terminal, the modification amount sometimes becomes small. Further, the amino group may be introduced both into a side chain and at the molecular chain terminal. The larger is the molecular weight of an amino-modified silicone, namely, the larger is the dynamic viscosity, the more improved is the heat resistance, and accordingly desired is an amino-modified silicone having a dynamic viscosity at 25°C of 1000 cSt or more, preferably 2000 cSt or more and more preferably 3000 cSt or more. The modification amount obtained by converting, in terms of the $-NH_2$ group, the amount of the terminal amino groups in the modifying groups is desired to be 0.05 to 10% by weight, preferably 0.1 to 5% by weight and more preferably 0.2 to 3% by weight. When the modification amount is less than 0.05% by weight, the affinity with the filament is sometimes insufficient, and when the modification amount exceeds 10% by weight, the heat resistance is sometimes decreased.

[0036]

As for the epoxy-modified silicone, the modifying group may be a glycidyl group or an alicyclic epoxy group; from the viewpoint of ensuring the affinity with the filament, preferable is the modification with an alicyclic epoxy group such as a 1,2-epoxycyclohexyl group or a 1,2-epoxycyclopentyl group. The epoxy group may be introduced into a side chain or at a molecular chain terminal. Further, the epoxy group may be introduced both into a side chain and at the molecular chain terminal. However, an epoxy-modified silicone with the epoxy groups introduced at both of the molecular chain terminals is preferable from the viewpoint of the reactivity of each of the epoxy groups. The larger is the molecular weight of an epoxy-modified silicone, namely, the larger is the dynamic viscosity, the more improved is the heat resistance, and accordingly desired is an epoxy-modified silicone having a dynamic viscosity at 25°C of 100 cSt or more, preferably 500 cSt or more and more preferably 1000 cSt or more. The modification amount obtained by converting, in terms of the $-CHCH_2O$

group, the amount of the terminal epoxy groups in the epoxy-modified silicone is desired to be 0.05 to 10% by weight, preferably 0.1 to 5% by weight and more preferably 0.2 to 3% by weight. When the modification amount is less than 0.05% by weight, the affinity with the filament is sometimes insufficient, and when the modification amount exceeds 10% by weight, the heat resistance is sometimes decreased.

[0037]

When an amino-modified silicone and an epoxy-modified silicone are combined, the mixing ratio between these silicones has an optimal point varying with the individual modification amounts of these silicones; a preferable condition is such that the number of moles of the amino group and that of the epoxy group are nearly equivalent to each other. In this connection, the ratio in which the proportion of the amino-modified silicone is slightly higher than that of the epoxy-modified silicone is preferable from the viewpoint of enhancing the affinity with the filament and the heat resistance of the silicone oiling agent. Accordingly, the weight ratio of the amino-modified silicone to the epoxy-modified silicone is desired to be 1:10 to 100:1, preferably 1:3 to 30:1, more preferably 1:2 to 10:1 and furthermore preferably 1:1 to 3:1.

[0038]

The higher the heat resistance of a silicone oiling agent to be imparted to a filament is the better. Accordingly, the heat-surviving rate r of such a silicone oiling agent is desired to be 20% by weight or more, preferably 30% or more and more preferably 40% or more. As matters stand now, it is difficult to make the heat-surviving rate r exceed 90%. The measurement of the heat-surviving rate r is based on a method to be described later.

[0039]

The adhesion amount of a silicone oiling agent to the filament is desired to be such that the oiling agent is imparted in an amount of 0.2 to 2% by weight in relation to the dry weight of the filament, preferably 0.4 to 1.6% by weight and more preferably 0.6 to 1.2% by weight.

[0040]

There are various methods for imparting an oiling agent to a filament such as an dipping method, a kiss roller method, a guided oiling method, a method based on a driven/nondriven roller in an oiling agent bath, a method in which the imparting is made to a traveling filament hung on a fixed/nonfixed guide bar, a method in which the imparting is made by making a filament travel through the upward jet of the oiling agent, a method in which the imparting is made to a traveling filament by dropping the oiling agent from the above, a method in which the imparting is made by making a filament travel through a space in which an oiling agent liquid is sprayed, and combinations of these methods. From these methods, an appropriate method can be selected according to the type and the application of the filament.

[0041]

Here, when the amount of the silicone oiling agent is too large, sometimes no sufficient resin adhesion is obtained for the carbon fiber to be obtained. Accordingly, it is preferable to keep to the minimum necessary the amount of the silicone oiling agent to be imparted and to make consideration so as to carry out uniform imparting to a filament on the basis of the above described methods.

[0042]

For the purpose of enhancing the uniform adhesiveness of an oiling agent to a filament, it is effective to convey a filament with two or more free rollers disposed side by side in a zigzag manner in such a way that the sum of the contact angles between the filament and the free rollers is 8π or more, after imparting oiling agent on the basis of the above described method. The larger is the sum of such contact angles, the effect is preferably higher; however, it is practical to constrain the sum of the contact angles to be 16π or less for the purpose of reducing the equipment cost and saving the space.

[0043]

Subsequently, the filament after having been drawn in a bath is dried with a hot drum or the like to dry and densify the filament. The drying temperature, the required time and the like can be appropriately selected.

[0044]

If needed, it is preferable to subject the filament, after having been dried and densified, to drawing in a higher-temperature environment such as drawing in pressurized steam.
[0045]

It is preferable to enhance as much as possible the drawing magnification after drying and densifying, from the viewpoint of processability, because the drawing magnification before drying and densifying is decreased as compared to the conventional method. Accordingly, such a drawing magnification is desired to be 3 or more, preferably 4 or more, more preferably 5 or more and furthermore preferably 6 or more. In many cases, such a drawing magnification of approximately 10 is sufficient to attain the advantageous effects of the present invention.
[0046]

By drying and densifying, the porous fibril structure present on the surface of a swollen filament loses its structure owing to the vanishment of the voids inside the swollen filament. Accordingly, even when drawing is carried out again after drying and densifying, the surface irregularities are not developed and the surface structure at the time of drying and densifying is maintained as it is.
[0047]

Further, it is preferable to impart a silicone straight oiling agent to a filament after drying and densifying. A silicone straight oiling agent can be imparted in advance of flame retardation in the firing step. The silicone straight oiling agent means a silicone oiling agent in which the water content in relation to the whole oiling agent is made to be 10% by weight or less. The water content exceeding 10% by weight sometimes unpreferably necessitates a drying step subsequent to the imparting of the oiling agent.
[0048]

For the purpose of obtaining a carbon fiber having a high strength, it is effective to use a precursor having a high densification. Such a precursor is desired to have a lightness difference ΔL as a measure of the densification, based on the iodine adsorption method, of 45 or less, preferably 35 or less and more preferably 30 or less. For the purpose of obtaining a high-densification precursor having a ΔL value of 45 or

less, it is preferable to suppress to a low level the swelling degree of the coagulated filament by making the spinning solution high in concentration, by decreasing the temperature of the spinning solution or the coagulation bath solution or by decreasing the tension at the time of coagulation, and also it is preferable to suppress to a low level the swelling degree of the filament after bath drawing by optimizing, at the time of bath drawing, the number of the drawing steps, the drawing magnification, the drawing temperature and the like. The densification of the precursor to be obtained can also be improved by decreasing the tension applied to the filament at the time of steam drawing after drying and densifying.

[0049]

The lightness difference ΔL can be measured by the following method. A well-dried precursor was cut to a fiber length of 5 to 7 cm; approximately 0.5 g of the cut precursor is weighed out accurately and is placed in a 200-ml stoppered Erlenmeyer flask; to the flask was added 100 ml of an aqueous solution of iodine (51 g of iodine, 10 g of 2,4-dichlorophenol, 90 g of acetic acid and 100 g of potassium iodide are dissolved in water using a 1-l measuring flask), and iodine is well adsorbed inside the fiber while the flask is being shaken at 60°C for 50 minutes. The iodine-adsorbed fiber is washed in flowing water for approximately 30 minutes, then centrifugally dehydrated (2000 rpm × 1 minute), and immediately thereafter dried in air. Further, the fiber is spread and then subjected to the L value (lightness) measurement by using a Hunter-type color difference meter (CM-25, manufactured by Color Machine Co., Ltd. is used here). The lightness thus obtained is designated as L_1. On the other hand, a fiber without iodine adsorbed therein is spread and the lightness thereof is measured with the above-mentioned color difference meter to yield a lightness which is designated as L_0. The difference between these two lightness values ($L_0 - L_1$) is defined as the lightness difference ΔL. From the viewpoint of improving the strength of the carbon fiber, it is desired to make the precursor have a fine fineness so that the firing unevenness may not occur in the subsequent flame retarding step. The monofilament fineness of the precursor is desired to be 1.5 d (d: denier) or less, preferably 1 d or less and more preferably 0.8 d or less.

[0050]

For the purpose of carrying out the subsequent firing step, with good through-passing ability, for firing involving no twist while preventing the fuzz generation and the filament breakage in the firing step, the precursor is desired to have a hook drop length of 20 cm or less, preferably 15 cm or less and more preferably 10 cm or less.

[0051]

By carrying out the above described production process, a precursor having a predetermined fineness and a predetermined orientation degree can be obtained, and after firing, a carbon fiber having a desired surface configuration can be obtained.

[0052]

As the flame retardation conditions, there are preferably adopted such conditions that the flame retardation is carried out in an oxidative atmosphere set at a range from 200 to 300°C by applying tension or drawing. The flame retardation is desired to be carried out until the specific gravity of the fiber becomes 1.25 or more and preferably 1.3 or more. The specific gravity is commonly set at 1.6 or less. When the specific gravity exceeds 1.6, sometimes the performance of the carbon fiber is impaired. As for the atmosphere in the flame retarding step, there can be adopted any of the oxidative atmospheres of air, oxygen, nitrogen dioxide and hydrogen chloride. An atmosphere of air is preferable because of low cost.

[0053]

When flame retardation unevenness is present in the fiber bundle or the single fiber of the flame retarded fiber, sometimes the strength or the tensile modulus of elasticity of the carbon fiber is degraded and the processability of the carbonizing step is adversely affected. As means for observing such flame retardation unevenness, there can be used a fact that with increasing flame retardation unevenness of the precursor, the solubility (hereinafter, abbreviated as formic acid solubility) of the precursor in formic acid is increased. The flame retardation is desired to be carried out in such a way that such a solubility comes to be 0.1 to 5% by weight. For the purpose of obtaining a high

performance carbon fiber, the solubility is preferably 3% by weight or less and more preferably 2% by weight or less.

[0054]

When fine solid particles are present on the surface of the precursor, voids tend to be formed between the monofilaments, such voids are effective for improving the diffusion of oxygen into the filament bundle, and the formic acid solubility can be decreased.   The diameter of such fine solid particles is desired to be 0.05 to 5 μm, preferably 0.07 to 3 μm and more preferably 0.1 to 1 μm.   The material for the fine solid particles may be either an organic compound or a silicone compound; however, organic fine particles are preferable because they are not too hard and hardly impart flaws to the precursor.   Particularly preferred among such organic materials are crosslinked polymethylmethacrylate and crosslinked polystyrene.   These fine particles are preferably imparted uniformly to the surface of the precursor before the flame retarding step; it is preferable to impart the fine particles by mixing the particles in the silicone oiling agent as an aqueous emulsion with the aid of an emulsifying agent or to impart, after the imparting of the oiling agent, by spraying or dropping a separately prepared mixture of these particles with an emulsifying agent.   Preferred as the emulsifying agent to be used for this purpose is a nonionic surfactant.

[0055]

The filament having been subjected to the flame retardation is carbonized according to an ordinary method in an inert atmosphere.   From the view point of enhancing the performance of the carbon fiber to be obtained, the atmospheric temperature concerned is desired to be 1000°C or higher, and preferably 1400°C or higher.   If needed, by further carbonizing at 2000°C or higher, the carbon fiber can be converted into a graphitized carbon, but sometimes the strength is degraded.   For the purpose of obtaining a carbon fiber sparse in defects inside the carbon fiber such as voids and high in densification, the temperature increase rate is desired to be 500°C/min or less, preferably 300°C/min or less and more preferably 150°C/min or less for the ranges from 350 to 500°C and from 1000 to 1200°C.   The temperature increase rate of 10°C/min or less degrades the productivity.   Further, for the purpose of

improving the densification of the carbon fiber, it is desired to draw at 350 to 500°C by 1% or more, preferably 5% or more and more preferably 10% or more. A drawing by more than 40% is not preferable because fuzz tends to be generated. From the viewpoint of improving the physical properties and the processability of the carbon fiber, it is preferable to carry out the carbonization with a plurality of furnaces allotted to different temperature ranges such as a low-temperature range of 600 to 1000°C relatively abundant in decomposition products and a temperature range thereabove. As described above, the silicone to be imparted to the precursor is preferably crosslinked for the purpose of obtaining a higher-performance carbon fiber.

[0056]

The carbon fiber thus obtained can be improved in the affinity between the carbon fiber and the matrix resin in a composite material and the resin adhesion by applying to the carbon fiber an electrolytic oxidation treatment in an electrolytic solution or an oxidation treatment in a vapor or liquid phase.

[0057]

Particularly preferred among these is the electrolytic oxidation treatment because the electrolytic oxidation treatment can carry out the oxidation treatment in a short time and can be easily controlled. There can be adopted either an acidic or an alkaline electrolytic solution for the electrolytic oxidation treatment. Examples of the electrolyte to be dissolved in an acidic electrolytic solution may include inorganic acids such as sulfuric acid and nitric acid; organic acids such as acetic acid and butyric acid; and salts such as ammonium sulfate and ammonium hydrogen sulfate. Preferably used among these are sulfuric acid and nitric acid that exhibit strong acidity. Examples of the electrolyte to be dissolved in an alkaline electrolytic solution may include hydroxides such as sodium hydroxide and potassium hydroxide; ammonia; inorganic salts such as sodium carbonate and sodium hydrogen carbonate; organic salts such as sodium acetate and sodium benzoate; potassium salts, barium salts and other metal salts and ammonium salts of these; and organic compounds such as tetraethylammonium hydroxide and hydrazine. From the viewpoint of preventing the curing failure of the

resin, preferably used among these are ammonium carbonate, ammonium hydrogen carbonate and tetraalkylammonium hydroxides, which contain no alkali metal.

[0058]

The electric charge to be used can be optimized according to the carbonization degree of the carbon fiber. From the viewpoint of appropriately suppressing the degradation of the crystallinity of the surface layer, such electric charge is set to fall within a range preferably from 3 to 500 coulomb/g and more preferably from 5 to 200 coulomb/g.

[0059]

After the electrolytic oxidation treatment, it is desired to wash with water and dry the filament. In drying, when the temperature is too high, the functional groups present on the outermost surface of the carbon fiber tend to be removed by thermal decomposition. Thus, the drying temperature is preferably set to be as low as possible, and the drying is desired to be carried out at 250°C or lower and preferably at 210°C or lower.

[0060]

Further, if needed, a sizing agent can also be imparted by an ordinary method. The carbon fiber according to the present invention is desired to have a spreadability index of 20 to 40. The spreadability index is desired to be preferably 25 to 40 and more preferably 30 to 40. The spreadability index indicates a spreading width per the weight of the fiber per unit length; the higher is this value, there can be produced a composite material that is the higher in the uniformity of the performance, the excellent performance of the carbon fiber is reflected in the properties of the composite material, and such properties can be enhanced. When the spreadability index is less than 20, it becomes difficult to obtain a composite material that has uniform properties, and such a small spreadability index is to be a cause for damaging of filaments because such a small spreadability index necessitates a width widening with the aid of a high pressure in order to ensure a sufficient filament width. When the spreadability index exceeds 40, sometimes the bundling property of the carbon fiber becomes insufficient, and the handling property in forming a composite material is degraded.

[0061]

For the purpose of making the spreadability index fall within a proper range, it is preferable to fire the precursor in a state substantially involving no twist. The state substantially involving no twist means that there is no twist exceeding 1 turn/m in the precursor. Such a twist is desired to be set preferably at a 0.5 turn/m or less. When there is a twist exceeding 1 turn/m in the precursor, sometimes it becomes difficult to obtain a carbon fiber having an appropriate spreadability index, and additionally sometimes the above described formic acid solubility is increased and the flame retardation reaction within the filament bundle possibly becomes nonuniform.

[0062]

The carbon fiber according to the present invention is desired to have a tensile modulus of elasticity in a resin-impregnated strand of 200 GPa or more, preferably 220 GPa or more, more preferably 240 GPa or more and furthermore preferably 280 GPa or more. If needed, the carbon fiber according to the present invention can be made to be a carbon fiber having a further higher tensile modulus of elasticity, but it is difficult, as the matters stand now, to make such a tensile modulus of elasticity be approximately 1020 GPa that is a theoretical value of graphite. The tensile modulus of elasticity set at less than 200 GPa is not preferable because sometimes no desired properties can be obtained in a composite material prepared with such a carbon fiber.

[0063]

The carbon fiber according to the present invention is desired to have a number-of-atoms ratio between Si and C (Si/C), obtained by SIMS, at the depth of 50 nm from the surface of the fiber is 1 or less. Herewith, Si in the surface layer is reduced in content to improve the strength, and a high resin adhesion can also be obtained. The number-of-atoms ratio (Si/C) is preferably 0.5 or less and more preferably 0.2 or less. As matters stand now, when a silicone oiling agent is used in the step concerned, it is difficult to set the number–of-atoms ratio (Si/C) at 0.001 or less.

[0064]

In the carbon fiber according to the present invention, the number-of-atoms ratio between Si and C (Si/C), obtained by ESCA, on the surface of the fiber is desired to be

0.01 or less. Herewith, silica on the surface is reduced and the resin adhesion can be improved. The number-of-atoms ratio (Si/C) is preferably 0.007 or less and more preferably 0.004 or less. The ESCA detection limit of the number-of-atoms ratio (Si/C) is approximately 0.001 as matters stand now.

[0065]

By combining, with an ordinary method, a carbon fiber obtained by such a method as described above with a matrix, there can be produced a prepreg that is an intermediate base material or a composite material that is a final product. Examples of the resin to be used as the matrix may include epoxy resin, phenolic resin, polyester resin, vinyl ester resin, bismaleimide resin, polyimide resin, polycarbonate resin, polyamide resin, polypropylene resin and ABS resin. In addition to the above described resins, cement, metals, ceramics and the like can also be used for the matrix.

[0066]

A prepreg can be used as a resin-impregnated sheet in which carbon fibers are aligned by pulling along one direction, namely, a unidirectional prepreg. A prepreg can also be used as a fabric prepreg which is prepared as follows: a fabric is prepared in advance from carbon fibers, and then the fabric is impregnated with a resin.

[0067]

A composite material can be fabricated by laminating the above described prepregs along optional directions and by thereafter curing them. Alternatively, a composite material can also be fabricated by the filament wind method in which filaments are wound while the filaments are being directly impregnated with a resin. Furthermore, a composite material can also be fabricated by the following methods: the sheet molding compound (SMC) method in which carbon fibers are in advance cut into chopped fibers and extruded under kneading with a resin and long fibers are pulled out together with the resin; and a method in which carbon fibers are once processed into chopped fibers or the like and then a composite material is fabricated by the hand lay up method, the press molding method, the autoclave method, the pultrusion method or the like.

[0068]

The composite material can be used for the following applications: primary and secondary structural materials for aircraft; sports goods such as a golf club shaft, a fishing rod, a snowboard and a ski stick; marine articles such as a yacht mast and a boat hull; general energy-related industrial applications such as a fly wheel, a CNG tank, a wind mill and a turbine blade; maintenance and repair materials for a road and a bridge pier; and building materials such as a curtain wall. Among these, the composite material can be suitably used for energy-related applications such as a fly wheel and a CNG tank by effectively making use of the advantages of the composite material according to the present invention that the composite material is highly resistant to failure and repetitive fatigue.

[0069]

Here, it should be noted that, in Examples to be described later, the values of the individual physical properties were measured by the following methods.

<Surface area ratio of a carbon fiber>

The carbon fiber to be measured is cut to a length of a few millimeters, fixed on a substrate (silicon wafer) with a silver paste; thus, a three-dimensional surface profile of the central portion of a single fiber is obtained by using Dimension 3000 stage system in an atomic force microscope (AFM), NanoScope IIIa, manufactured by Digital Instruments, and under the below described conditions.

[0070]

* Scanning mode: Tapping mode

* Probe: OMCL-AC120TS probe integrated with Si cantilever, manufactured by Olympus Optical Co., Ltd.

* Scanning range: 2.5 μm $\times$ 2.5 μm

* Scanning speed: 0.4 Hz

* Number of pixels: 512 $\times$ 512

* Measurement environment: Room temperature, in atmosphere.

For each of the samples, an image is obtained from one position of a single fiber. Such an image is subjected to data processing with a software (NanoScope III, version 4.22r2) adjunct to the above described apparatus, subjected to filtering with a primary

Flatten filter, a Lowpass filter and a tertiary Plane Fit filter, and for the whole image thus obtained, the real surface area and the projected area are calculated. The projected area is an area projected onto a three-dimensional curved surface that is an approximation made by considering the fiber section curvature. The surface area ratio is derived from the following equation. For each of the samples, five arbitrarily selected positions are subjected to the above described measurement, the maximum and the minimum of the five measured values thus obtained are discarded, and the arithmetic average of the remaining values for three positions is defined as the final surface area ratio.

Surface area ratio = Real surface area/Projected area

[0071]

<Root-mean-square roughness Rq of three-dimensional roughness>

An original image obtained by the above described method using an AFM is subjected to data processing with a software adjunct to the above described apparatus to derive a three-dimensional approximate curved surface by considering the fiber section curvature. The root-mean-square roughness is derived by subtracting the three-dimensional approximate curved surface as the background from the original image. Five arbitrary positions are subjected to the same measurement, the maximum and the minimum of the five measured values thus obtained are discarded, and the arithmetic average of the remaining values for three positions is defined as the final root-mean-square roughness Rq of the three-dimensional roughness.

[0072]

<Tensile strength and tensile modulus of elasticity of carbon fiber>

A carbon fiber to be measured is impregnated with a resin composition prepared by mixing together 1000 g (100 parts by weight) of Bakelite (registered trademark) ERL-4221 manufactured by Union Carbide Corp., 30 g (3 part by weight) of boron trifluoride-monoethylamine (BF$_3$·MEA) and 40 g (4 parts by weight) of acetone. Then, curing is made by heating at 130°C for 30 minutes to yield a resin-impregnated strand. The tensile strength and the tensile modulus of elasticity are obtained according to the resin-impregnated strand test method (JIS R7601).

[0073]

<ILSS>

A resin composition is prepared by mixing together 3.5 kg (35 parts by weight) of Epicoat (registered trademark) 1001 manufactured by Yuka-Shell Epoxy Co., Ltd., 2.5 kg (25 parts by weight) of Epicoat 828 manufactured by the same company, 3.0 kg (30 parts by weight) of Epiclon (registered trademark) N740 manufactured by Dainippon Ink and Chemicals, Inc., 1.5 kg (15 parts by weight) of Epicoat 152 manufactured by Yuka-Shell Epoxy Co., Ltd., 0.8 kg (8 parts by weight) of Denka Formal (registered trademark) #20 manufactured by Denki Kagaku Kogyo Kabushiki Kaisha and 0.5 kg (5 parts by weight) of dichlorophenyl dimethylurea, and by stirring this mixture for 30 minutes. The resin composition thus obtained is coated on a release paper coated with silicone to yield a resin film.

[0074]

Then, the above described resin film is wound around a circular copper drum, of 2.7 m in circumference, heated so as for the surface temperature to be 60 to 70°C; then, carbon fibers wound off from a creel stand are arranged on the resin film while being taken up through a traverse with the circular drum; the resin film is covered with another sheet of the above described resin film; the laminate thus obtained is subjected to roll-pressed with a pressure roll to impregnate the resin into the inside of the fiber bundle; and thus there is fabricated a prepreg that has a fiber weight per unit area of approximately 200 g/m² and a resin content of approximately 35% by weight while the rotational speed of the drum and the feed speed of the traverse are being varied appropriately. This prepreg is laminated so as for the fiber direction to be constant, the laminate is cured at 135°C for 2 hours under a pressure of approximately 2.9×10^5 Pa, to fabricate a composite material piece having a width of 200 mm, a length of 250 mm and a thickness of 2 mm. From this material piece, a test piece having a width of 12.7 mm and a length of seven times the thickness is cut out. The test piece is subjected to a breaking load measurement with an ordinary three-point bending test jig under the conditions that the support span is set at four times the test piece thickness and the

strain speed is set at 1.27 mm/min. The average value (n = 8) is defined as the breaking load to be derived from the following equation.

ILSS (MPa) = 0.75 × (breaking load)/{(test piece thickness) × (test piece width)}

[0075]

<0° Tensile strength>

Tensile strength measurement is carried out according to ASTM D3039-76. A prepreg is fabricated in the same manner as in the ILSS measurement method. This prepreg is laminated so as for the fiber direction to be constant, the laminate is cured at 135°C for 2 hours under a pressure of approximately 2.9×10^5 Pa, to fabricate a composite material piece having a width of 200 mm, a length of 250 mm and a thickness of 1 mm. The gauge length is set at 127 mm, and at each of both ends thereof an approximately 50 mm long and 1 mm thick tab made of a glass fiber composite material is adhered. From this material piece, a test piece having a width of 12.7 mm and a length of 230 mm is cut out. The test piece is subjected to a breaking load measurement with an ordinary tensile test jig at a strain speed set at 2 mm/min. The fiber volume fraction Vf is set at 60%, and the 0° tensile strength is derived using the obtained value from the following equation.

0° tensile strength = (breaking load) × 60/{(test piece thickness) × (test piece width) × (fiber volume fraction Vf)}

Here, the breaking load is an average value over the values obtained by measuring six test pieces, and the fiber volume fraction Vf (%) is a value obtained from the following equation.

Fiber volume fraction Vf (%) = 10 × Y × p × n/(d × t)

In this equation:

Y: Weigh of carbon fiber per unit length (g/m)

p: Carbon fiber number density (number/cm) at the time of prepreg fabrication

n: Prepreg laminate number at the time of preparing a test piece

d: Carbon fiber density (g/cm³)

t: Test piece thickness (mm)

[0076]

<Number-of-atoms ratio between Si and C (Si/C) at the depth of 50 nm from the surface>

The value of this ratio is measured by SIMS.   The carbon fibers to be measured are aligned and are subjected to a measurement of secondary ions generated by irradiating primary ions to the side of the fibers in an environment of a vacuum with the following measurement apparatus under the following measurement conditions; thus, (Si/C) is the ratio between the obtained count number of silicon and the obtained count number of carbon at the depth of 50 nm from the surface of the carbon fibers.
[0077]

- Apparatus: A-DIDA 3000 manufactured by ATOMIKA AG, Germany
- Primary ion species: O^{2+}
- Primary ion energy: 12 keV
- Primary ion current: 100 nA
- Raster area: 250 × 250 μm
- Gate rate: 30%
- Analysis area: 75 × 75 μm
- Detected secondary ion: Positive ion
- Electron spray conditions: 0.6 kV − 3.0 A (F7.5)
- Degree of vacuum at measurement: 1×10^{-6} Pa
- H-Q-H: #14

[0078]

<Number-of-atoms ratio between Si and C (Si/C) on the surface of a fiber>

The value of this ratio is measured by ESCA.   When a sizing agent is adhered to the carbon fibers to be measured, the sizing agent is removed by the pretreatment method described below.
[0079]

The sample is subjected to a 2-hour reflux carried out with a Soxhlet extractor by using a 2:1 (weight ratio) mixed solution of methanol and chloroform.   Thereafter, the sample is soaked in sulfuric acid at room temperature for 12 hours, then fully washed with methanol, and dried in air.   Subsequently, with the following measurement

apparatus and under the following measurement conditions, the peak area ratio between the Si_{2P} peak and the C_{1S} peak to be observed at around 100 eV is derived; the measured values are multiplied by an apparatus constant of 0.814 to give the number-of-atoms ratio (Si/C).

[0080]

- Apparatus: ESCA 750 manufactured by Shimadzu Corp.
- Excitation X-ray: $K\alpha_{1,2}$-ray of Mg
- Binding energy of C_{1S} main peak: 284.6 eV

[0081]

<Hook drop length>

There is beforehand prepared a piece of stainless steel wire of approximately 3 cm in length and approximately 0.5 mm in diameter which is crooked in a hook shape so as for the diameter of the circular arc portion to be 5 mm, and a 5 g of weight is fixed to one end thereof.

[0082]

The precursor to be measured is sampled in a length of approximately 1 m, and one end thereof is fixed and a weight of 500 g/per 12000 monofilaments is fixed to the other end. Then, the precursor is hung in an appropriate place.

[0083]

The above described hook portion is inserted in the center of the fiber bundle portion 5 cm below the fixed upper end of the precursor and is gently released. The hook portion falls vertically due to its own weight and the displacement distance as observed until the hook portion comes to rest is measured. Such a measurement is repeated at least 10 times, and the arithmetic average value obtained therefrom is defined as the hook drop length.

[0084]

<Heat-surviving rate r of an oiling agent>

In an aluminum vessel of approximately 60 mm in diameter and approximately 20 mm in height, approximately 1 g of an oiling agent to be measured is sampled and placed, and dried in an oven at 105°C for 5 hours. The substance thus obtained is

subjected to a measurement in air at 240°C for 120 minutes, and then a measurement in nitrogen at 450°C for 30 minutes under the following conditions with a thermogravimetric balance (TG). The total weight retention rate in the thermogravimetric balance is defined as the heat-surviving rate r.

- Sample pan: Made of aluminum, diameter: 5 mm, height: 5 mm
- Sample quantity: 15 to 20 mg
- Heat treatment in air (procedure 1)

Air flow rate: 30 ml/min

Temperature increase rate: 10°C/min (range: room temperature to 240°C)

Heat treatment time (240°C): 120 minutes

- Atmosphere alteration (procedure 2)

Altering from air to nitrogen and keeping for 5 minutes while maintaining at 240°C

- Heat treatment in nitrogen (procedure 3)

Nitrogen flow rate: 30 ml/min

Temperature increase rate: 10°C/min (range: 240 to 450°C)

Heat treatment time (450°C): 30 minutes

[0085]

<Swelling degree of a filament>

A sample of approximately 10 g of swollen filaments before drying and densifying is the measurement sample. The swelling degree of a filament is derived from the weight w (g) after compulsorily removing the moisture adhering to the surface of the sample with a centrifugal dehydrator at 3000 rpm for 15 minutes, and the weight w_0 (g) after drying the dehydrated sample at 110°C for 2 hours with a hot air dryer, on the basis of the following equation.

Swelling degree of a filament (%) = $(w - w_0) \times 100/w_0$

[0086]

<Formic acid solubility of a flame retarded fiber>

A sample of approximately 2.5 g of a flame retarded fiber is dried at 120°C for 2 hours with a hot air oven or the like, and then the weight of the sample after drying is accurately weighed to give Gp (g). The sample after drying is placed in a 200-cc

beaker, 100 cc of formic acid having a purity of 90 to 100% is poured into the beaker, and the beaker is shaken at 25°C for 100 minutes for treatment. Thereafter, the sample was taken out, washed in flowing water for 60 minutes, and then washed in heated water at 90°C for 2 hours. Further, the sample is dried at 120°C for 2 hours, and the weight after drying is accurately weighed to give Gl(g). From these obtained values, the formic acid solubility (%) is derived on the basis of the following equation.

Formic acid solubility (%) = {(Gp − Gl)/Gp} × 100

[0087]

<[η] of a polymer>

A dried sample of 75 mg of an acrylic polymer to be measured is placed in a 25-ml measuring flask, a 0.1-N dimethylformamide solution of sodium thiocyanate is poured into the flask so as to reach the marked line, and dissolution is carried out completely. Thereafter, the sample solution is subjected to a measurement of the specific viscosity η_{sp} at 25°C with an Ostwald viscometer. From the specific viscosity η_{sp}, [η] is derived on the basis of the following equation.

$$[\eta] = \{(1 + 1.32\, \eta_{sp})^{1/2} - 1\}/0.198$$

[0088]

<Flame shrinkage retention rate of a flame retarded fiber>

A sample of a flame retarded fiber is sampled in a length of approximately 40 cm, and two points are marked with nonflammable articles such as clips so that the distance between the two points gives a test length of 20 cm. Then, one end of the sample is fixed, a tensile of 10 g/per 3000 d is applied from the other end, and the sample filaments are heated with a flame of a Bunsen burner. In this heating, by regulating the air supply to the Bunsen burner, a reductive yellow flame is generated, and the heating is made by one and a half round trip between the marks at a speed of 15 sec/20 cm. The length of the filaments between the marks after the heating is denoted by Wb (mm), and the flame shrinkage retention rate (%) is derived on the basis of the following equation.

Flame shrinkage retention rate (%) = (Wb/200) × 100

[0089]

<Spreadability index of a carbon fiber>

A carbon fiber bundle having the number of monofilaments of 3000 or more is adopted as a sample.   The carbon fiber bundle is taken out from the creel stand by applying a tension of 1000 gf per the number of monofilaments of 12000, impregnated with Epicoat (registered trademark) 828 manufactured by Yuka-Shell Epoxy Co., Ltd., and thereafter wound around, while being traversed at a constant speed, a circular rotatable steel drum the surface of which is covered with a release paper and which has a diameter of 730 mm and the width of 500 mm.   After the drum is rotated a few revolutions, the fiber width in the state of being wound is measured in units of 0.1 mm. The arithmetic average (n = 30) is denoted by W (mm), and the weight of the carbon fiber as the sample per 1 m is denoted by Gm (g).   The spreadability index is derived on the basis of the following equation.

Spreadability index = W/Gm

[0090]

[Examples]

Hereinafter, further specific description will be made on the present invention with reference to Examples.   Table 1 shows the yarn-making conditions, the firing conditions and the main data for the precursors.   Table 2 shows the main data for the carbon fibers and the composite materials.

[0091]

(Example 1)

By the solution polymerization method using dimethylsulfoxide as solvent, there was obtained a spinning solution that contained 22% by weight of a polymer consisting of 97.6% by weight of acrylonitrile (AN) and 2.4% by weight of itaconic acid, and having a [η] value of 1.7.   After polymerization, ammonia gas was blown into the solution until the pH became 8.5 to neutralize the itaconic acid and to introduce ammonium groups into the polymer, and the hydrophilicity of the spinning solution was thereby improved. The temperature of the obtained spinning solution was set at 70°C, and a wet spinning method was applied.   By using a spinneret that had an orifice diameter of 0.065 mm and the number of orifices of 6000, the spinning solution was extruded to be coagulated

directly into a coagulation bath composed of a 60% by weight aqueous solution of dimethylsulfoxide, the coagulation bath being regulated in temperature at 70°C.
[0092]

Then, the coagulated filament was drawn in heated water at 75, 85 and 95°C so as for the total drawing magnification to be 2, and then washed with water at 50°C. The swelling degree of the drawn-in-bath filament was 200%.
[0093]

Then, to the drawn-in-bath filament, there was imparted a silicone-based oiling agent that was a mixture consisting of an amino-modified silicone, an epoxy-modified silicone and an ethylene oxide-modified silicone. The viscosities at 25°C of the amino-modified, epoxy-modified and ethylene oxide-modified silicones were 4000 cSt, 12000 cSt and 500 cSt, respectively, and the mixing ratio between these silicones was 10:10:1 (weight ratio). The heat-surviving rate r of the oiling agent was 42%.
[0094]

Further, drying and densifying were carried out with a hot roller regulated in temperature at 180°C.
[0095]

After drying and densifying, further drawing was carried out in pressurized steam of 3 kg/cm^2-G to attain a total drawing magnification of 13. Then, three filaments were combined, and subjected to an intermingling treatment with pressurized air set at 1 kg/cm^2-G to yield a precursor that had a single fiber fineness of 0.8 d (d: denier) and the number of monofilaments of 18000. The ΔL (lightness difference) of the precursor was 26.
[0096]

The fiber bundle thus obtained was heated, as it was in a state involving no twist, in air at 240 to 280°C with a drawing magnification of 1.0, to be converted into a flame retarded fiber that had a flame shrinkage retention rate of 78% and a formic acid solubility of 1.1%. Further, the flame retarded fiber was subjected to a preliminary carbonization in an inert atmosphere at 300 to 900°C with a drawing magnification of 1.04, and then carbonized wherein the maximum temperature was 1500°C.

[0097]

Thereafter, the carbonized fiber was subjected to an electrolytic oxidation treatment of 20 coulomb/g-CF in an aqueous solution of ammonium bicarbonate to yield a carbon fiber. The obtained carbon fiber was extremely satisfactory in grade and exhibited high performance.

[0098]

(Example 2)

A carbon fiber was obtained in the same manner as in Example 1 except that no intermingling treatment with pressurized air of 1 kg/cm^2-G was carried out. Much fuzz was found in the firing step, but the obtained carbon fiber exhibited satisfactory performance.

[0099]

(Example 3)

A carbon fiber was obtained in the same manner as in Example 1 except that the drawing magnifications in flame retardation and preliminary carbonization were set at 0.95 and 1.0, respectively, and the maximum temperature in the carbonization was set at 1700°C. The obtained carbon fiber was extremely satisfactory in grade and exhibited high performance.

[0100]

(Comparative Example 1)

A carbon fiber was obtained in the same manner as in Example 1 except that the drawing magnification in the heated water bath was set at 5. It is to be noted that, in the present Comparative Example, the swelling degree of the drawn-in-bath filament was increased up to 260%. The performance of the obtained carbon fiber was somewhat inferior.

[0101]

(Comparative Example 2)

A carbon fiber was obtained in the same manner as in Comparative Example 1 except that no intermingling treatment with pressurized air of 1 kg/cm^2-G was carried

out. Fuzz was generated in the firing step and the fabrication was abandoned before completion.

[0102]

(Comparative Example 3)

A carbon fiber was obtained in the same manner as in Example 1 except that the drawing magnifications in flame retardation and preliminary carbonization were set at 0.95 and 1.0, respectively, and the maximum temperature in the carbonization was set at 1700°C. The performance of the obtained carbon fiber was somewhat inferior.

[0103]

(Comparative Example 4)

By the solution polymerization method using dimethylsulfoxide as solvent, there was obtained a spinning solution that contained 22% by weight of a polymer consisting of 98.8% by weight of acrylonitrile (AN) and 1.2% by weight of itaconic acid, and having a [η] value of 1.7. After polymerization, ammonia gas was blown into the solution until the pH became 8.5 to neutralize the itaconic acid and to introduce ammonium groups into the polymer, and the hydrophilicity of the spinning solution was thereby improved. The temperature of the obtained spinning solution was set at 70°C, and a dry-wet spinning method was applied. By using a spinneret that had an orifice diameter of 0.15 mm and the number of orifices of 6000, the spinning solution was once extruded into air, and then guided to be coagulated into a coagulation bath consisting of a 40% aqueous solution of dimethylsulfoxide, the coagulation bath being regulated in temperature at 10°C.

[0104]

The coagulated filament thus obtained was washed with water, and then drawn in heated water at 70, 80 and 90°C so as for the total drawing magnification to be 4. The swelling degree of the drawn-in-bath filament was 80%.

[0105]

Then, to the drawn-in-bath filament, there was imparted a silicone oiling agent that was a mixture consisting of an amino-modified silicone, an epoxy-modified silicone and an ethylene oxide-modified silicone. The viscosities at 25°C of the amino-modified,

epoxy-modified and ethylene oxide-modified silicones were 4000 cSt, 12000 cSt and 500 cSt, respectively, and the mixing ratio between these silicones was 10:10:1 (weight ratio). The heat-surviving rate r of the oiling agent was 42%.

[0106]

Further, drying and densifying were carried out with a hot roller regulated in temperature at 180°C.

[0107]

After drying and densifying, further drawing was carried out in pressurized steam of 3 kg/cm²-G to attain a total drawing magnification of 13. Then, three filaments were combined to yield a precursor that had a single fiber fineness of 0.8 d and the number of monofilaments of 18000.

[0108]

A carbon fiber was obtained by further carrying out the same firing step as in Comparative Example 1. The performance of the obtained carbon fiber was somewhat inferior.

[0109]

(Example 4)

By the solution polymerization method using dimethylsulfoxide as solvent, there was obtained a spinning solution that contained 18% by weight of a polymer consisting of 94.9% by weight of acrylonitrile (AN), 1.2% by weight of itaconic acid and 3.9% by weight of isobutyl methacrylate, and having a [η] value of 1.8. After polymerization, ammonia gas was blown into the solution until the pH became 8.5 to neutralize the itaconic acid and to introduce ammonium groups into the polymer, and the hydrophilicity of the spinning solution was thereby improved. The temperature of the obtained spinning solution was set at 70°C, and a wet spinning method was applied. By using a spinneret that had an orifice diameter of 0.07 mm and the number of orifices of 12000, the spinning solution was extruded to be coagulated directly into a coagulation bath consisting of a 60% by weight aqueous solution of dimethylsulfoxide, the coagulation bath being regulated in temperature at 70°C.

[0110]

Then, the coagulated filament was drawn in heated water at 75, 85 and 95°C so as for the total drawing magnification to be 2, and then washed with water at 50°C. The swelling degree of the drawn-in-bath filament was 205%.

[0111]

Then, to the drawn-in-bath filament, there was imparted a silicone oiling agent composed of an amino-modified silicone. The viscosity at 25°C of the amino-modified silicone was 4000 cSt. The heat-surviving rate r of the oiling agent was 25%.

[0112]

Further, drying and densifying were carried out with a hot roller regulated in temperature at 180°C.

[0113]

After drying and densifying, further drawing was carried out in pressurized steam of 3 kg/cm^2-G to attain a total drawing magnification of 13. Then, filaments were subjected to an intermingling treatment with pressurized air set at 1.5 kg/cm^2-G to yield a precursor that had a single fiber fineness of 1.1 d and the number of monofilaments of 12000.

[0114]

The fiber bundle thus obtained was heated, as it was in a state involving no twist, in air at 240 to 280°C with a drawing magnification of 0.95, to be converted into a flame retarded fiber that had a flame shrinkage retention rate of 85% and a formic acid solubility of 1.5%. Further, the flame retarded fiber was subjected to a preliminary carbonization in an inert atmosphere at 300 to 900°C with a drawing magnification of 1.0, and then carbonized wherein the maximum temperature was 1300°C.

[0115]

Thereafter, the carbonized fiber was subjected to an electrolytic oxidation treatment of 10 coulomb/g-CF in an aqueous solution of ammonium bicarbonate to yield a carbon fiber. The obtained carbon fiber was extremely satisfactory in grade and exhibited high performance.

[0116]

(Example 5)

A carbon fiber was obtained in the same manner as in Example 4 except that there was used, as a polymer, a copolymer consisting of 98.8% by weight of acrylonitrile (AN) and 1.2% by weight of itaconic acid. The obtained carbon fiber was extremely satisfactory in grade and exhibited high performance.

[0117]

(Example 6)

A carbon fiber was obtained in the same manner as in Example 4 except that the drawing magnifications in flame retardation and preliminary carbonization were set at 0.90 and 0.95, respectively. The obtained carbon fiber was extremely satisfactory in grade and exhibited high performance.

[0118]

(Comparative Example 5)

A carbon fiber was obtained in the same manner as in Example 4 except that the drawing magnification in the heated water bath was set at 5. The performance of the obtained carbon fiber was somewhat inferior.

[0119]

(Comparative Example 6)

A carbon fiber was obtained in the same manner as in Example 5 except that the drawing magnifications in flame retardation and preliminary carbonization were set at 0.90 and 0.95, respectively. The performance of the obtained carbon fiber was somewhat inferior.

[0120]

(Comparative Example 7)

By the solution polymerization method using dimethylsulfoxide as solvent, there was obtained a spinning solution that contained 22% by weight of a polymer consisting of 98.8% by weight of acrylonitrile (AN) and 1.2% by weight of itaconic acid, and having a [η] value of 1.7. After polymerization, ammonia gas was blown into the solution until the pH became 8.5 to neutralize the itaconic acid and to introduce ammonium groups into the polymer, and the hydrophilicity of the spinning solution was thereby improved. The temperature of the obtained spinning solution was set at 70°C, and a dry-wet

spinning method was applied. By using a spinneret that had an orifice diameter of 0.15 mm and the number of orifices of 6000, the spinning solution was once extruded into air, and then guided to be coagulated into a coagulation bath consisting of a 40% aqueous solution of dimethylsulfoxide, the coagulation bath being regulated in temperature at 10°C.

[0121]

Then, the coagulated filament was washed with water, and then drawn in heated water at 70, 80 and 90°C so as for the total drawing magnification to be 4. The swelling degree of the drawn-in-bath filament was 80%.

[0122]

Then, to the drawn-in-bath filament, there was imparted a silicone oiling agent that was a mixture consisting of an amino-modified silicone, an epoxy-modified silicone and an ethylene oxide-modified silicone. The viscosities at 25°C of the amino-modified, epoxy-modified and ethylene oxide-modified silicones were 4000 cSt, 12000 cSt and 500 cSt, respectively, and the mixing ratio between these silicones was 10:10:1 (weight ratio). The heat-surviving rate r of the oiling agent was 42%.

[0123]

Further, drying and densifying were carried out with a hot roller regulated in temperature at 180°C.

[0124]

After drying and densifying, further drawing was carried out in pressurized steam of 4 kg/cm^2-G to attain a total drawing magnification of 13. Then, two filaments were combined to yield a precursor that had a single fiber fineness of 1.1 d and the number of monofilaments of 12000.

[0125]

A carbon fiber was obtained by further carrying out the same firing step as in Comparative Example 6. The performance of the obtained carbon fiber was somewhat inferior.

[0126]

(Comparative Example 8)

A carbon fiber was obtained in the same manner as in Comparative Example 7 except that there was used, as a polymer, a copolymer consisting of 94.9% by weight of acrylonitrile (AN), 1.2% by weight of itaconic acid and 3.9% by weight of isobutylmethacrylate. The performance of the obtained carbon fiber was somewhat inferior.

[0127]

[Table 1]

	Drawing-in-bath magnification (times)	Single fiber fineness (d)	Number of filaments	Hook drop length (cm)	Flame retardation drawing ratio	Formic acid solubility (%)	Preliminary carbonization drawing ratio	Carbonization temperature (°C)
Example 1	2.0	0.8	18000	10	1.00	1.1	1.04	1500
Example 2	2.0	0.8	18000	30	1.00	1.2	1.04	1500
Example 3	2.0	0.8	18000	10	0.95	0.9	1.00	1700
Comparative Example 1	5.0	0.8	18000	8	1.00	1.0	1.04	1500
Comparative Example 2	5.0	0.8	18000	30	1.00	-	-	-
Comparative Example 3	5.0	0.8	18000	8	0.95	0.8	1.00	1700
Comparative Example 4	4.0	0.8	18000	30	1.00	1.5	1.04	1500
Example 4	2.0	1.1	12000	12	0.95	1.5	1.00	1300
Example 5	2.0	1.1	12000	12	0.95	2.5	1.00	1300
Example 6	2.0	1.1	12000	12	0.90	1.4	0.95	1300
Comparative Example 5	5.0	1.1	12000	10	0.95	1.4	1.00	1300
Comparative Example 6	5.0	1.1	12000	10	0.90	1.3	0.95	1300

[Table 2]

	Tensile strength (GPa)	Modulus of elasticity (GPa)	Surface area ratio	Root-mean-square Rq of 3-dimen-sional roughness (nm)	Spreadability index	0° Tensile strength (GPa)	ILSS (Mpa)	Si/C (at 50 nm depth)	Si/C (ESCA)
Example 1	6.3	296	1.05	17	24	3.2	97	0.2	0.003
Example 2	6.1	294	1.05	18	25	3.0	97	0.2	0.003
Example 3	6.0	298	1.04	16	30	3.0	98	0.1	0.000
Comparative Example 1	5.4	294	1.10	30	24	2.8	98	1.1	0.003
Comparative Example 2	-	-	-	-	-	-	-	-	-
Comparative Example 3	5.2	295	1.10	28	29	2.6	93	0.6	0.000
Comparative Example 4	6.3	295	1.00	3	24	3.2	83	0.1	0.010
Example 4	5.8	244	1.07	22	21	3.0	99	0.4	0.009
Example 5	5.5	238	1.06	21	22	2.8	99	0.4	0.008
Example 6	5.5	230	1.07	20	23	2.8	99	0.4	0.009
Comparative Example 5	4.5	240	1.12	31	21	2.2	100	1.0	0.011
Comparative Example 6	4.2	222	1.13	30	24	2.1	99	1.0	0.012

[0128]

[Advantages of the Invention]

The carbon fiber of the present invention permits obtaining a carbon fiber-reinforced composite material unprecedentedly light in weight, high in performance and excellent in cost performance. Such a composite material can be suitably used for energy related applications such as a rotor of a fly wheel and a CNG tank, and for a primary structural material of aircraft.

[0129]

The production method of the precursor of the present invention enables obtaining, inexpensively and easily, a high-performance carbon fiber which allows two properties, namely, the strength and the resin adhesion to be compatible with each other.

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(54)【発明の名称】　炭素繊維、及び炭素繊維用プリカーサーの製造方法

(57)【要約】

【課題】高性能かつ安価な複合材料を製造するのに好適
な、強度と樹脂接着性に優れる炭素繊維、及び炭素繊維
用プリカーサーの製造方法を提供すること。

【解決手段】表面積比が1．02～1．09である炭素
繊維、及び、湿式紡糸法において、膨潤度が50量％以
上である糸条を4倍以下で延伸する工程を含む、炭素繊
維用プリカーサーの製造方法。

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【特許請求の範囲】

【請求項１】表面積比が１．０２～１．０９であることを特徴とする炭素繊維。

【請求項２】引張強度が５．５ＧＰａ以上、かつ層間剪断強度が９０ＭＰａ以上であることを特徴とする請求項１記載の炭素繊維。

【請求項３】湿式紡糸法により得られるアクリル系繊維をブリカーサーとする請求項１又は２記載の炭素繊維。

【請求項４】ＳＩＭＳにより求まる、繊維表面から５０ｎｍの深さ部におけるＳｉとＣとの原子数比（Ｓｉ／Ｃ）が１以下である請求項１～３のいずれかに記載の炭素繊維。

【請求項５】ＥＳＣＡにより求まる、繊維表面におけるＳｉとＣとの原子数比（Ｓｉ／Ｃ）が０．０１以下である請求項１～４のいずれかに記載の炭素繊維。

【請求項６】拡がり性指数が２０～４０である請求項１～５のいずれかに記載の炭素繊維。

【請求項７】フックドロップ長が２０ｃｍ以下であるブリカーサーを焼成して得られるものである請求項１～６のいずれかに記載の炭素繊維。

【請求項８】湿式紡糸法において、糸条を紡出した後、その膨潤度が５０～３００重量％である状態で４倍以下で延伸し、その後乾燥緻密化して得られることを特徴とする炭素繊維用ブリカーサーの製造方法。

【請求項９】湿式紡糸法において、糸条を紡出した後、その膨潤度を２２５重量％以下に保持した状態で延伸し、その後乾燥緻密化して得られることを特徴とする炭素繊維用ブリカーサーの製造方法。

【請求項１０】請求項１～７のいずれかに記載の炭素繊維から得られる、強度特性に優れた炭素繊維強化複合材料。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、強度と樹脂との接着性を両立し、かつコストパフォーマンスに優れた炭素繊維、及び炭素繊維用ブリカーサーの製造方法に関する。

【０００２】

【従来の技術】炭素繊維は他の繊維に比べて優れた比強度及び比弾性率を有するため、その軽量性と、優れた機械的特性を利用して樹脂と共に複合材料を製造する際の補強材として工業的に広く利用されている。近年、炭素繊維強化複合材料の優位性はますます高まり、特にスポーツ、航空宇宙用途において、炭素繊維と、炭素繊維強化複合材料に対する、さらなる高性能化が要求されている。

【０００３】炭素繊維は、その殆どが、その表面に存在する微小な欠陥（以下、表面欠陥と略記）が開始点となって破断しており、そのため、炭素繊維の高性能化を図るためには、かかる表面欠陥の生成を極力抑えるよう、

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製造工程において配慮する必要がある。表面欠陥を、発生後に除去する方法としては、特開昭５８－２１４５２７号公報、特開昭６１－２２５３３０号公報に、炭素繊維に気相処理、液相処理、電解酸化処理などの後処理を施すことにより、表層部分をエッチング処理して表面欠陥を強制除去する方法が提案されている。

【０００４】しかし、これら方法によれば、得られる炭素繊維の強度は向上するものの、操作、工程が非常に煩雑となり、製造コストも大幅に上昇するため、実際の生産技術としては採用が困難であった。炭素繊維は、高性能化とともに、一層の低価格化への要望も大きく、コストパフォーマンスの高い炭素繊維でないと市場に受け入れられないというのが現状である。

【０００５】湿式紡糸法により、炭素繊維用ブリカーサーを製造する場合は、湿式紡糸法に特徴的に発生するフィブリル構造の凹凸部から破断が開始し、強度を損なっている場合が多い。そこで特開昭６２－１４１１２４号公報には、乾湿式紡糸法を採用して、凝固張力を下げることによりかかる凹凸部を低減する方法が提案されている。

【０００６】しかし、この方法によれば、得られる炭素繊維の強度は向上するものの、繊維表面の凹凸部が減少することによって、樹脂との接着性が低下し、補強繊維としての炭素繊維の特性を存分に発揮できない場合があった。

【０００７】一方、近年、エネルギー関連用途として、電力需要の平準化や無停電電源用に高い性能を有するフライホイールが、二酸化炭素の排出削減のため、圧縮天然ガス（ＣＮＧ）自動車が開発されつつあり、各々ローター、ガス貯蔵用タンクの素材として炭素繊維の採用が予定されている。

【０００８】これら用途は主に炭素繊維の、優れた引張強度特性を利用するものであるが、ローターでは高速回転時に半径方向に遠心力で膨張変形し、繊維と樹脂を引き剥がそうとする力に耐えるため、また、ガス貯蔵用タンクでは、ガスの充填と放出による繰り返し疲労後の特性の悪化や、物体が衝突した後の残存強度の劣化を防止するため、それぞれ引張強度と共に樹脂との高い接着性が要求されている。

【０００９】上記事情を背景として、高い引張強度を有しながら、樹脂との高い接着性を確保した炭素繊維と、該炭素繊維が安価かつ容易に得られる製造方法が強く要望されている。

【００１０】

【発明が解決しようとする課題】本発明の課題は、通常はトレードオフの関係である、炭素繊維の引張強度と樹脂との接着性を高いレベルで両立しながら、かつコストパフォーマンスにも優れる炭素繊維、及び炭素繊維用ブリカーサーの製造方法を提供することにある。さらには、かかる炭素繊維を使用することにより、強度特性に

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優れた炭素繊維強化複合材料を製造することにある。

【００１１】
【課題を解決するための手段】本発明の炭素繊維は、上記課題を解決するために次の構成を有する。すなわち、表面積比が１．０２～１．０９である炭素繊維である。

【００１２】また、本発明の炭素繊維用プリカーサーの製造方法は、上記課題を達成するために次のいずれかの構成を有する。すなわち、湿式紡糸法において、糸条を紡出した後、その膨潤度が５０～３００重量％である状態で４倍以下で延伸し、その後乾燥緻密化して得られることを特徴とする炭素繊維用プリカーサーの製造方法、又は、湿式紡糸法において、糸条を紡出した後、その膨潤度を２２５重量％以下に保持した状態で延伸し、その後乾燥緻密化して得られることを特徴とする炭素繊維用プリカーサーの製造方法である。

【００１３】
【発明の実施の形態】発明者らは、炭素繊維の表面形態に着目し、その制御を適切に行うことによって、通常は相反する特性である、０°引張強度に代表される強度特性（以下、単に強度と略記）と層間剪断強度に代表される樹脂との接着性（以下、単に樹脂接着性と略記）とを両立できることを見出し、本発明に至った。

【００１４】本発明の炭素繊維は、乾湿式紡糸法によって得られるような表面が非常に平滑な炭素繊維と、湿式紡糸法によって得られるような表面に凹凸部を多く有する炭素繊維との中間の表面形態を有するものである。すなわち、本発明の炭素繊維は、高い強度を有するという前者の特徴と、高い樹脂接着性を有するという後者の特徴を兼ね備えた、高い性能を有するものである。以下、本発明について詳細に説明する。

【００１５】本発明の炭素繊維は、表面積比が１．０２～１．０９であることを特徴とするものである。従来、表面が平滑と云われる炭素繊維の表面積比は、通常、１以上１．０２未満の範囲にあり、かかる炭素繊維は、強度には優れるが、樹脂接着性に劣っていた。一方、表面に凹凸部が多いと云われる炭素繊維の表面積比は、通常、１．０９を超えるものであり、樹脂接着性には優れるが、強度に劣っていた。　そこで、発明者らが鋭意検討を重ねた結果、表面積比が１．０２～１．０９の範囲にある炭素繊維が、強度と樹脂接着性を高いレベルで両立することが判明した。表面積比は、１．０２５～１．０８であれば、強度と樹脂接着性の両立に当たり好ましい結果が得られる。かかる観点より、表面積比は、より好ましくは１．０３～１．０７、さらに好ましくは１．０３５～１．０６が良い。

【００１６】表面積比の他に、炭素繊維の表面形態を定量化する指標として、三次元粗さの二乗平均粗さＲｑが採用できる。この指標によれば、強度と樹脂接着性の両立に当たり、Ｒｑは１０～２４ｎｍが良く、好ましくは１３～２３ｎｍ、より好ましくは１６～２２ｎｍが良

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い。

【００１７】また、本発明による炭素繊維の引張強度については、炭素繊維強化複合材料（以下、単に複合材料と略記）の性能を高めるために、５．５ＧＰａ以上であることが好ましく、より好ましくは５．７ＧＰａ以上、さらに好ましくは６ＧＰａ以上、特に好ましくは６．５ＧＰａ以上であることが良い。引張強度は、１０ＧＰａ程度あれば本発明の効果を奏するに充分であることが多い。また、本発明における炭素繊維のＩＬＳＳは、複合材料の特性を高めるために、９０ＭＰａ以上であることが好ましく、より好ましくは９２ＭＰａ以上、さらに好ましくは９４ＭＰａ以上、特に好ましくは９６ＭＰａ以上であることが良い。ＩＬＳＳは、１２０ＭＰａ程度あれば本発明の効果を奏するに充分であることが多い。

【００１８】本発明による炭素繊維は、アクリル系、ピッチ系、レーヨン系などいずれの由来でも良い。特に、アクリル系の炭素繊維用プリカーサー（以下、単にプリカーサーと略記）を、後述するような望ましい方法と条件により紡糸して得た後、焼成して得られるものである。紡糸法としては、湿式紡糸法が好ましいが、乾湿式紡糸法や乾式紡糸法でも良い。本発明において焼成とは、製糸工程で得られたプリカーサーを、耐炎化に引き続いて予備炭化及び炭化して最終生産物たる炭素繊維とする一連の処理をいう。以下にプリカーサーを湿式紡糸法により製造する方法を例として、本発明の炭素繊維の製造方法について説明する。

【００１９】プリカーサーの原料としては、アクリロニトリルを８５重量％以上含み、アクリロニトリルと共重合可能な重合性不飽和単量体を１５重量％以下含む重合体が好適に使用される。重合性不飽和単量体の具体例としては、アクリル酸、メタクリル酸、イタコン酸、及びそれらのアルカリ金属塩、並びにアクリル酸、メタクリル酸、イタコン酸、及びそれらのアンモニウム塩、並びにアクリル酸、メタクリル酸、イタコン酸、及びそれらのアルキルエステル類、並びにアクリルアミド、メタクリルアミド及びそれらの誘導体、並びにアリルスルホン酸、メタリルスルホン酸及びそれらの塩類、並びにアルキルエステル類などが挙げられる。

【００２０】耐炎化反応を促進するためには、前記重合性不飽和単量体に不飽和カルボン酸などを共重合させるのが良い。その共重合量は、重合体全体に対して、０．１～１０重量％が良く、好ましくは０．３～５重量％、より好ましくは０．５～３重量％が良い。不飽和カルボン酸の具体例としては、アクリル酸、メタクリル酸、イタコン酸、クロトン酸、シトラコン酸、エタクリル酸、マレイン酸、メサコン酸などが挙げられ、中でもアクリル酸、メタクリル酸、イタコン酸が好ましい。

【００２１】得られる炭素繊維の強度を極力向上させるためには、前記重合性不飽和単量体に不飽和カルボン酸のアルキルエステル、酢酸ビニルから選ばれた１種以上

を共重合させるのが良い。その共重合量は、重合体全体に対して、０．１～１０重量％が良く、好ましくは０．３～５重量％、より好ましくは０．５～３重量％が良い。不飽和カルボン酸のアルキルエステルの具体例としては、アクリル酸メチル、メタクリル酸メチル、メタクリル酸プロピル、メタクリル酸ブチル、メタクリル酸イソブチル、メタクリル酸セカンダリーブチルなどを挙げることができるが、その中でもアクリル酸、メタクリル酸のプロピル、ブチル、イソブチル、セカンダリーブチルエステルが好ましい。

【００２２】重合体を得る際の重合法としては、懸濁重合法、溶液重合法、乳化重合法など、を採用することができる。重合体の重合度としては、極限粘度（以下、［η］と略記）基準で、１以上が良く、好ましくは１．２５以上、より好ましくは１．５以上が良い。なお、［η］は高々５以下とするのが紡糸安定性の点から好ましい。

【００２３】かかる重合体を溶媒に溶解してなる重合体溶液を紡糸原液として用いる。重合体溶液に使用する溶媒としては、有機、又は無機の溶媒が使用できるが、紡糸原液を、口金を介して直接凝固浴中へ紡出する湿式紡糸法による場合は、有機溶媒が好ましい。具体的には、ジメチルスルホキシド、ジメチルホルムアミド、ジメチルアセトアミドなどが挙げられる。硝酸、ロダンソーダ水溶液、塩化亜鉛水溶液などの無機塩の濃厚水溶液をである無機溶媒を用いると、所望する表面形態の炭素繊維を得られないときがある。

【００２４】凝固浴中に紡出後、糸条を水洗しないで直接、延伸浴中で延伸しても良いし、溶媒を水洗して除去した後に延伸浴中で延伸しても良い。かかる延伸浴は、通常、５０～９８℃に温調された温水からなり、また前記溶媒の濃度が０重量％から凝固浴の濃度までの範囲になるよう設定される。

【００２５】本発明において、得られる炭素繊維の表面形態に最も影響を及ぼすのは、プリカーサーを製造する製糸工程、特に乾燥緻密化前の糸条が膨潤状態にあるときに延伸する条件であるため、これに特に注意する必要がある。

【００２６】乾燥緻密化前に、浴中で糸条が膨潤状態にあるときの延伸倍率が高過ぎると、糸条表面の凹凸部の発現が過剰となる傾向があるため、目標とする適切な表面形態を有する炭素繊維を得るには、乾燥緻密化前の糸条の膨潤度が５０～３００重量％にある状態で、延伸倍率を４倍以下として延伸することが必要である。より高い強度を有する炭素繊維を得るために、かかる延伸倍率は、好ましくは３倍以下、より好ましくは２．５倍以下、さらに好ましくは２倍以下とするのが良い。

【００２７】かかる延伸倍率は、少なくとも１．１倍程度ないと、プリカーサーの製造工程全体での延伸性を確保できなくなることがある。

【００２８】従来、かかる延伸倍率を低くすると、生産性が低下し製造コストが上昇するため、延伸倍率を低くする条件は採用し難いものがあったが、後述するように乾燥緻密化後の延伸倍率を適正化することによって、プリカーサーの製造工程全体での延伸性は意外にも低下することなく、生産性の低下や製造コスト上昇を伴わずに高い性能を有する炭素繊維を得ることができる。

【００２９】また、延伸浴中での糸条の延伸倍率が高めの場合、糸条の膨潤度が上昇する領域が認められ、かかる領域において糸条表面の凹凸部が多く発生しており、かかる状態の糸条を延伸すると、プリカーサー及び炭素繊維における表面の凹凸部の発現が顕著となることが判明した。したがって、所望する適切な表面形態を有する炭素繊維を得るには、延伸浴中での糸条の膨潤度を、延伸する際に２２５重量％以下に保持し、かかる表面の凹凸部の発現を抑制することが必要である。かかる糸条の膨潤度は２１５重量％以下が好ましく、２０５重量％以下がより好ましい。なお、ホットローラーとの接触による加熱などによって特別に乾燥操作を施すことなく糸条の膨潤度を５０重量％未満とするのは現状では困難である。

【００３０】延伸浴の温度が高めの場合は、入り側ローラーによる熱圧着のため、単繊維間の接着が起こり易いため、入り側ローラーは延伸浴から外に出すのが良い。また、単繊維間での弱い接着を解除するために、延伸浴中に振動ガイドを設けて、糸束を振動させながら延伸するのが良い。その際の振動数としては、５～１００Ｈｚが良く、振幅は０．１～１０ｍｍが良い。

【００３１】また、本発明によるプリカーサーは、従来の湿式紡糸法により得られるプリカーサーと比較して表面が平滑なため、乾燥緻密化時や焼成工程において単糸間接着が発生し易いため、乾燥緻密化に先立って、糸条にシリコーン油剤を付与するのが良い。ここで、シリコーン油剤は、エマルジョンの形態で付与するのが好ましい。また、アルキレンオキサイド変性シリコーンをシリコーン油剤に含ませるのが、乳化安定性を高める観点から好ましい。アルキレンオキサイド変性シリコーンについては、エチレンオキサイド変性、プロピレンオキサイド変性、又は両者で変性されているものが好ましい。アルキレンオキサイドで変性することによって、シリコーン油剤に適度な親水性が付与され、自己乳化性を付与して界面活性剤に類似する機能を持たせることができる。

【００３２】かかる処理により、シリコーン油剤に、水中における安定性や糸条表面への均一な付着性など、望ましい特性が生じるものと考えられる。また、シリコーンのアルキレンオキサイドによる変性量は、１０～８０重量％が良く、好ましくは２０～７０重量％が良い。１０重量％未満では、自己乳化性が不足することがあり、また、８０重量％を超えると耐熱性が低下することがある。

【００３３】アルキレンオキサイドのユニット（＝繰り返し単位）数は、シリコーン油剤の耐熱性を確保する観点から、２５個以下が好ましい。また、シリコーンは分子量が大きい程、即ち動粘性率が大きい程、耐熱性が向上するため、２５℃における動粘性率は１００ｃＳｔ以上のものが良く、好ましくは２００ｃＳｔ以上、より好ましくは３００ｃＳｔ以上のものが良い。なお、動粘性率が１００００ｃＳｔを超えると水中に分散させることが困難になる場合がある。

【００３４】さらにアルキレンオキサイド変性シリコーンに加え、アミノ変性シリコーン又は／及びエポキシ変性シリコーンを組み合せることもできる。

【００３５】アミノ変性シリコーンについては、モノアミン型でもポリアミン型でも良い。ここでアミノ基は側鎖に導入されていても良く、また、分子鎖末端に導入されていても良いが、分子鎖末端のみの変性の場合、変性量が小さくなることがある。さらには側鎖と分子鎖末端の両方に導入されていてもよい。アミノ変性シリコーンは分子量が大きい程、即ち動粘性率が大きい程、耐熱性が向上するため、２５℃における動粘性率が１０００ｃＳｔ以上のものが良く、好ましくは２０００ｃＳｔ以上、より好ましくは３０００ｃＳｔ以上のものが良い。また、変性基の末端アミノ基を－ＮＨ,と換算した変性量は、０．０５～１０重量％が良く、好ましくは０．１～５重量％、より好ましくは０．２～３重量％が良い。０．０５重量％未満では糸条との親和性が不足することがあり、１０重量％を超えると耐熱性が低下することがある。

【００３６】エポキシ変性シリコーンについては、グリシジル基でも脂環式エポキシ基でも良いが、糸条との親和性を確保する観点から、１，２－エポキシシクロヘキシル基や１，２－エポキシシクロペンチル基のような脂環式エポキシ変性が好ましい。ここでエポキシ基は側鎖に導入されていても良く、また、分子鎖末端に導入されていても良い。さらには側鎖と分子鎖末端の両方に導入されていてもよいが、分子鎖両側の末端に導入されているものが、エポキシ基の反応性の観点から好ましい。エポキシ変性シリコーンは、分子量が大きい程、即ち動粘性率が大きい程、耐熱性が向上するため、２５℃における動粘性率が１００ｃＳｔ以上のものが良く、好ましくは５００ｃＳｔ以上、より好ましくは１０００ｃＳｔ以上のものが良い。エポキシ変性シリコーンの末端エポキシ基を－ＣＨＣＨ,Ｏと換算した変性量は、０．０５～１０重量％が良く、好ましくは０．１～５重量％、より好ましくは０．２～３重量％が良い。０．０５重量％未満では糸条との親和性が不足することがあり、１０重量％を超えると耐熱性が低下することがある。

【００３７】アミノ変性シリコーンとエポキシ変性シリコーンとを組み合わせる場合は、それらの混合比率はそれぞれの変性量によっても最適点が異なるが、アミノ基

とエポキシ基のモル数が当量に近い状態が良い。ここでエポキシ変性シリコーンよりアミノ変性シリコーンの比率が高めの方が、糸条との親和性とシリコーン油剤の耐熱性を高める観点から好ましい。したがって、アミノ変性シリコーンとエポキシ変性シリコーンとの重量比は１：１０～１００：１が良く、好ましくは１：３～３０：１、より好ましくは１：２～１０：１、さらに好ましくは１：１～３：１が良い。

【００３８】糸条に付与するシリコーン油剤の耐熱性は高い程良い。したがって、かかるシリコーン油剤の加熱残存率ｒは、２０重量％以上が良く、好ましくは３０％以上、より好ましくは４０％以上が良い。現状では加熱残存率ｒを９０％を超えるようにすることは困難である。加熱残存率ｒの測定は、後述する方法による。

【００３９】また、シリコーン油剤の糸条への付着量は、糸条の乾燥重量当たり０．２～２重量％になるよう付与するのが良い。好ましくは０．４～１．６重量％、より好ましくは０．６～１．２重量％が良い。

【００４０】糸条に油剤を付与する方法には、浸漬法、キスローラー法、ガイド給油法、油剤浴中の駆動・非駆動ローラーによる方法、固定・非固定のガイドバーへ走行する糸条を掛けて付与する方法、上方へ吹き出した油剤中に糸条を走行させて付与する方法、走行する糸条へ上方から油剤を滴下させて付与する方法、油剤液を噴霧した空間に糸条を走行させて付与する方法、又はこれらを複数組み合わせた方法など、多様な付与方法があり、これら方法から糸条の種類や用途に応じて適宜選択することができる。

【００４１】ここで、シリコーン油剤の量が多すぎると、得られる炭素繊維に充分な樹脂接着性が得られない場合があるため、付与するシリコーン油剤の量は必要最小限に止め、前記付与方法により糸条へ均一に付与するよう配慮するのが好ましい。

【００４２】糸条への油剤の均一付着性をより高めるためには、前記方法により油剤を付与した後に、糸条がフリーローラーとなす接触角の総和が８π以上になるように、ジグザグに複数個配置して並べたフリーローラーで糸条を搬送させることが有効である。かかる接触角の総和は、大きいほど効果が高く好ましいが、設備コストの低減及び省スペースを図るため、１６π以下とするのが実用的である。

【００４３】次いで、浴中延伸後の糸条を、ホットドラムなどで乾燥することによって乾燥緻密化する。ここでの乾燥温度、所要時間などは適宜選択することができる。

【００４４】また、必要に応じて乾燥緻密化後の糸条を、加圧スチーム中で延伸するなどして、より高温の環境で延伸するのが好ましい。

【００４５】乾燥緻密化後の延伸倍率は、乾燥緻密化前の延伸倍率を従来法と比較して低下させているため、極

力高くする方がプロセス性の観点から好ましい。したがって、かかる延伸倍率は、３倍以上が良く、好ましくは４倍以上、より好ましくは５倍以上、さらに好ましくは６倍以上が良い。なおかかる延伸倍率は１０倍程度有れば、本発明の効果を奏するに充分であることが多い。

【００４６】乾燥緻密化により、膨潤糸表面に存在する多孔質のフィブリル構造は、膨潤糸内部のボイドの消失により無構造化するため、乾燥緻密化後に再延伸を行っても表面の凹凸部は発達せず、乾燥緻密化の時点そのままの表面構造が維持される。

【００４７】さらに乾燥緻密化後の糸条にシリコーンストレート油剤を付与するのが好ましい。シリコーンストレート油剤は、焼成工程において耐炎化に先立って付与することもできる。シリコーンストレート油剤とは、油剤全体に対する含水比率を１０重量％以下としたシリコーン油剤をいう。含水比率が１０重量％を超えると、油剤付与後に乾燥工程が必要となる場合があり好ましくない。

【００４８】高い強度を有する炭素繊維を得るためには、緻密性の高いプリカーサーを用いることが有効である。かかるプリカーサーは、緻密性の尺度となる、ヨウ素吸着法による明度差△Ｌが、４５以下のものが良く、好ましくは３５以下、より好ましくは３０以下のものが良い。△Ｌが４５以下の緻密性の高いプリカーサーを得るためには、紡糸原液の高濃度化、紡糸原液もしくは凝固浴液の低温化、又は凝固時の低張力化などにより凝固糸の膨潤度を低く抑えると共に、浴延伸時に延伸する段数、延伸倍率及び延伸温度の最適化などにより浴延伸後の糸条の膨潤度を低く抑えるのが好ましい。乾燥緻密化後のスチーム延伸時に糸条に架かる張力を下げることによっても得られるプリカーサーの緻密性を向上させることができる。

【００４９】前記明度差△Ｌについては、次に示す方法により測定できる。よく乾燥させたプリカーサーを、繊維長５～７ｃｍとして約０．５ｇ精秤し、２００ｍｌの共栓付三角フラスコに採り、これにヨウ素水溶液（ヨウ素：５１ｇ、２、４－ジクロロフェノール１０ｇ、酢酸９０ｇ及びヨウ化カリウム１００ｇを、１１のメスフラスコを使用して水で溶解させたもの）１００ｍｌを加えて、６０℃、５０分間振盪しながら、ヨウ素をよく繊維中に吸着させる。ヨウ素を吸着した繊維を流水中で約３０分間水洗後、遠心脱水（２０００ｒｐｍ×１分）して直ちに風乾せしめる。さらに繊維を開繊後、ハンター型色差計（ここでは、カラーマシン（株）製、ＣＭ－２５型を使用）で、Ｌ値（明度）を測定する。これをＬ₁とする。一方、ヨウ素の吸着のない繊維を開繊後、前記の色差計で測定した明度を、Ｌ。として、両者の差分（Ｌ。－Ｌ₁）を明度差△Ｌとする。プリカーサーは、炭素繊維の強度向上の観点から引き続く耐炎化工程で焼成ムラを起こさないよう細繊度とするのが良い。プリカーサー

の単繊維繊度としては１．５ｄ（ｄ：デニール）以下が良く、好ましくは１ｄ以下、より好ましくは０．８ｄ以下が良い。

【００５０】また、プリカーサーは、続く焼成工程における毛羽立ち、糸切れなどを防止して無撚の焼成を工程通過性良く行うため、フックドロップ長が２０ｃｍ以下であるのが良い。フックドロップ長は、好ましくは１５ｃｍ以下、より好ましくは１０ｃｍ以下が良い。

【００５１】上述のような製造プロセスを経ることにより、所定の繊度、配向度を有するプリカーサーが得られ、焼成後に所望の表面形態を有する炭素繊維を得ることができる。

【００５２】耐炎化条件としては、酸化性雰囲気中２００～３００℃の範囲で、緊張又は延伸する条件が好ましく採用され、繊維の比重が１．２５以上、好ましくは１．３以上になるまで耐炎化するのが良い。この比重については、１．６以下とするのが一般的であり、これを超えると、炭素繊維の性能が損なわれることがある。また、耐炎化工程における雰囲気については、空気、酸素、二酸化窒素、塩化水素などの各酸化性雰囲気を採用できるが、空気雰囲気がローコストであり、好ましい。

【００５３】耐炎化糸の糸束や単糸内部に耐炎化ムラが存在すると、炭素繊維の強度や引張弾性率が低下したり、炭化工程のプロセス性に悪影響を及ぼすときがある。かかる耐炎化ムラを観測する手段として、プリカーサーの耐炎化ムラが増加するにつれ、そのギ酸への溶解度（以下、ギ酸溶解度と略記）が高くなることを利用して、かかる溶解度が０．１～５重量％となるように耐炎化するのが良い。溶解度は、３重量％以下であることが、高性能の炭素繊維を得るに当たって好ましく、２重量％以下であることがより好ましい。

【００５４】固体微粒子がプリカーサー表面に存在すると、単繊維間に空間が生じ易くなり、糸束内への酸素の拡散向上に有効であり、ギ酸溶解度を低下させることができる。かかる固体微粒子の径としては、０．０５～５μｍが良く、好ましくは０．０７～３μｍ、より好ましくは０．１～１μｍが良い。固体微粒子の材質としては、有機系の化合物又はシリコーン化合物のいずれでも良いが、硬さが硬すぎず、プリカーサーに傷を与えにくい有機系の微粒子が好ましい。かかる有機系の材質の中で、特に架橋ポリメチルメタクリレート、架橋ポリスチレンが好ましい。これら微粒子は、耐炎化工程の前に、プリカーサー表面に均一に付与するのが好ましく、乳化剤により水系のエマルジョンとしてシリコーン油剤に混合して付与するか、又は、油剤付与後に、別途、乳化剤と混合して噴霧又は滴下することにより、付与するのが好ましい。この際の乳化剤としては、ノニオン系界面活性剤が好ましい。

【００５５】耐炎化を完了した糸条は、常法により、不活性雰囲気中で炭化する。ここでの雰囲気温度は、得ら

れる炭素繊維の性能を高める観点から、１０００℃以上が良く、１４００℃以上が好ましい。さらに必要に応じて２０００℃以上で炭化して、黒鉛化繊維とすることもできるが、強度は低下することがある。また、ボイドなど、炭素繊維内部の欠陥の少ない、緻密性の高い炭素繊維を得るために、３５０～５００℃及び１０００～１２００℃における昇温速度は、５００℃／分以下が良く、好ましくは３００℃／分以下、より好ましくは１５０℃／分以下が良い。昇温速度が１０℃／分以下では生産性が低下してしまう。さらにまた、炭素繊維の緻密性を向上させるためには、３５０～５００℃において、１％以上、好ましくは５％以上、より好ましくは１０％以上延伸するのが良い。なお、４０％を超える延伸は毛羽が発生し易くなるため好ましくない。比較的分解発生物が多い６００～１０００℃までの低温部分とそれ以上の温度領域の複数の炉に分けて炭化することが、炭素繊維の物性向上、プロセス性向上の観点から好ましい。また、上述したような、プリカーサーに付与されるシリコーンは、架橋していることが、より高い性能の炭素繊維を得るに当たって好ましい。

【００５６】こうして得られた炭素繊維は、電解液中で電解酸化処理を施したり、気相又は液相での酸化処理によって、複合材料における炭素繊維とマトリックス樹脂との親和性や、樹脂接着性を向上させることができる。

【００５７】特に、短時間で酸化処理することができ、酸化処理のコントロールも容易なことから電解酸化処理が好ましい。電解酸化処理の電解液としては酸性、アルカリ性、いずれも採用できる。酸性の電解液に溶存させる電解質の具体例としては、硫酸、硝酸などの無機酸、酢酸、酪酸などの有機酸、硫酸アンモニウム、硫酸水素アンモニウムなどの塩が挙げられる。中でも強酸性を示す硫酸、硝酸が好ましく使用できる。アルカリ性の電解液に溶存させる電解質の具体例としては、水酸化ナトリウム、水酸化カリウムなどの水酸化物、アンモニア、炭酸ナトリウム、炭酸水素ナトリウムなどの無機塩類、酢酸ナトリウム、安息香酸ナトリウムなどの有機塩類、さらにこれらのカリウム塩、バリウム塩又は他の金属塩、及びアンモニウム塩、水酸化テトラエチルアンモニウム又はヒドラジンなどの有機化合物が挙げられるが、樹脂の硬化障害を防止する観点から、アルカリ金属を含まない炭酸アンモニウム、炭酸水素アンモニウム、水酸化テトラアルキルアンモニウム類が好ましく使用できる。

【００５８】通電する電気量は、炭素繊維の炭化度に応じて最適化することができる。表層の結晶性の低下を適度に抑える観点から、かかる電気量は３～５００クーロン／ｇ、さらには５～２００クーロン／ｇの範囲とするのが好ましい。

【００５９】電解酸化処理の後、糸条を水洗及び乾燥するのが良い。乾燥に際しては、温度が高過ぎると炭素繊維の最表面に存在する官能基が熱分解により消失しやす

いため、乾燥温度はできる限り低くするのが望ましく、２５０℃以下、好ましくは２１０℃以下で乾燥するのが良い。

【００６０】さらに、必要に応じて常法により、サイジング剤を付与することもできる。また、本発明による炭素繊維は、その拡がり性指数が２０～４０であることが良い。拡がり性指数は、好ましくは２５～４０、より好ましくは３０～４０であることが良い。拡がり性指数は、繊維目付当たりの糸の拡がり幅を示しており、この値が高い程、均一な性能の複合材料を製造でき、炭素繊維の優れた性能を、複合材料の特性に反映し、かかる特性を高めることができる。拡がり性指数が２０を下回ると、均一な特性の複合材料が得難くなり、工程において、十分な糸幅を確保するために高い圧力で拡幅することにもなり、糸を損傷する原因ともなる。拡がり性指数が４０を超えると、炭素繊維の集束性が不足し、複合材料を成型する際のハンドリング性が悪くなることがある。

【００６１】拡がり性指数を適正な範囲とするためには、プリカーサーを実質的に無撚の状態で焼成するのが好ましい。実質的に無撚の状態とは、プリカーサーに１ターン／ｍを超える撚りが存在しないことを意味する。かかる撚りは、好ましくは、０．５ターン／ｍ以下が良い。プリカーサーに１ターン／ｍを超える撚りが存在すると、適正な拡がり性指数を有する炭素繊維を得るのが困難になることがあるだけでなく、前記ギ酸溶解度が高くなり、糸束内部における耐炎化反応が不均一になることもある。

【００６２】本発明による炭素繊維は、樹脂含浸ストランドにおける引張弾性率が２００ＧＰａ以上のものが良く、好ましくは２２０ＧＰａ以上、より好ましくは２４０ＧＰａ以上、さらに好ましくは２８０ＧＰａ以上のものが良い。また必要に応じてさらに高い引張弾性率の炭素繊維とすることもできるが、かかる引張弾性率を、黒鉛の理論値である１０２０ＧＰａ程度とするのは現状では困難である。引張弾性率が２００ＧＰａ未満であると、複合材料とした場合、所望の特性が得られないときがあり好ましくない。

【００６３】また、本発明による炭素繊維は、ＳＩＭＳにより求まる、繊維表面から５０ｎｍの深さ部におけるＳｉとＣとの原子数比（Ｓｉ／Ｃ）が１以下であることが良い。これにより、表層のＳｉを減少して強度を向上させるとともに、高い樹脂接着性を得ることができる。かかる原子数比（Ｓｉ／Ｃ）は、０．５以下であることが好ましく、０．２以下であることがより好ましい。シリコーン油剤を工程で使用する場合、かかる原子数比（Ｓｉ／Ｃ）を０．００１以下とするのは現状では困難である。

【００６４】また、本発明による炭素繊維は、ＥＳＣＡにより求まる、繊維表面におけるＳｉとＣとの原子数比

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（Ｓｉ／Ｃ）が０．０１以下であることが良い。これにより、表面のシリカを減少して樹脂接着性を向上させることができる。かかる原子数比（Ｓｉ／Ｃ）は、０．００７以下であることが好ましく、０．００４以下であることがより好ましい。かかる原子数比（Ｓｉ／Ｃ）の、ＥＳＣＡの検出限界は、現状、０．００１程度である。

【００６５】このような方法で得られた炭素繊維を、常法により、マトリックスと組み合わせて、中間基材であるプリプレグや、最終生産品である複合材料とすることができる。マトリックスとして使用する樹脂としては、エポキシ樹脂、フェノール樹脂、ポリエステル樹脂、ビニルエステル樹脂、ビスマレイミド樹脂、ポリイミド樹脂、ポリカーボネート樹脂、ポリアミド樹脂、ポリプロピレン樹脂、ＡＢＳ樹脂などが挙げられる。また、マトリックスには、前記樹脂以外に、セメント、金属、セラミックスなどを使用することもできる。

【００６６】プリプレグは、炭素繊維を一方向に引き揃えた樹脂含浸シート、すなわち、一方向プリプレグとして使用でき、また、予め炭素繊維を織物にしておいてから、樹脂含浸する織物プリプレグとしても使用できる。

【００６７】複合材料は、前記プリプレグを任意の方向に積層して硬化せしめることによって製造でき、また、直接樹脂を含浸しながら巻き付けるフィラメントワインド法によっても製造できる。さらに、複合材料は、予め炭素繊維をチョップドファイバーにカットしておき、樹脂と混練しながら押し出す、長繊維を樹脂と共に引き抜く、シートモールデイングコンパウンド（ＳＭＣ）法、又は、チョップドファイバーなどに一旦加工した後に、ハンドレイアップ法、プレス成形法、オートクレーブ法、プルトルージョン法などの方法により製造することもできる。

【００６８】前記複合材料は、航空機の一次・二次構造材料、ゴルフシャフト、釣竿、スノーボード、スキーストックなどのスポーツ用品、ヨットのマスト、舟艇のハルなどのマリーン用品、フライホイール、ＣＮＧタンク、風車、タービンブレードなどのエネルギー関連の一般産業用途、道路・橋脚などの補修・補強材、カーテンウォールなどの建築用材料として用いることができるが、中でもエネルギー関連用途のフライホイール、ＣＮＧタンクなどに、高度の耐破壊特性と耐繰り返し疲労特性を有する本発明による複合材料の利点を活かして、好適に用いることができる。

【００６９】なお、後述する実施例においては、各物性値は以下に示す方法で測定した。＜炭素繊維の表面積比＞測定する炭素繊維を長さ数ｍｍ程度にカットし、銀ペーストを用いて基板（シリコンウエハ）上に固定し、Digital Instruments社製　NanoScope IIIa原子間力顕微鏡（ＡＦＭ）においてDimension 3000ステージシステムを使用し、下記条件にて、単糸の中央部について３次元表面形状の像を得る。

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【００７０】・走査モード：タッピングモード
・探針：オリンパス光学工業製Ｓｉカンチレバー一体型探針OMCL-AC120TS
・走査範囲：２．５μm×２．５μm
・走査速度：０．４Hz
・ピクセル数：５１２×５１２
・測定環境：室温、大気中

各試料について、単糸１本から１箇所ずつ観察して得られた像について、前記装置に付属のソフトウエア（NanoScope IIIバージョン4.22r2）によりデータ処理し、１次Flattenフィルタ、Lowpassフィルタ、３次Plane Fitフィルタを用いてフィルタリングし、得られた像全体を対象として実表面積と投影面積を算出する。なお、投影面積については、繊維断面の曲率を考慮し近似した３次曲面への投影面積とする。表面積比は次式で求める。各試料について、任意に選んだ５箇所について上記の測定を行い、最大値、最小値を除いた３カ所の相加平均値を最終的な表面積比とする。

表面積比＝実表面積／投影面積

【００７１】＜三次元粗さの二乗平均粗さＲｑ＞上記の方法に従いＡＦＭにより得られた原像について、前記装置に付属のソフトウエアによりデータ処理し、繊維断面の曲率を考慮した３次元近似曲面を求める。原像からこの３次元近似曲面をバックグラウンドとして差し引き、二乗平均粗さを求める。任意の５箇所について同様の測定を行い、最大値、最小値を除いた３カ所の相加平均値を最終的な三次元粗さの二乗平均粗さＲｑとする。

【００７２】＜炭素繊維の引張強度、引張弾性率＞測定する炭素繊維に、ユニオン・カーバイド（株）製　、ベークライト（登録商標）ＥＲＬ－４２２１を１０００ｇ（１００重量部）、三フッ化ホウ素モノエチルアミン（ＢＦ₃・ＭＥＡ）を３０ｇ（３重量部）及びアセトンを４０ｇ（４重量部）混合した樹脂組成物を含浸させ、次に１３０℃で、３０分間加熱して硬化させ、樹脂含浸ストランドを得る。樹脂含浸ストランド試験法（ＪＩＳ　Ｒ７６０１）により引張強度と引張弾性率を求める。

【００７３】＜ＩＬＳＳ＞油化シェルエポキシ社製、エピコート（登録商標）１００１を３．５ｋｇ（３５重量部）、同社製、エピコート８２８を２．５ｋｇ（２５重量部）と大日本インキ化学工業社製、エピクロン（登録商標）Ｎ７４０を３．０ｋｇ（３０重量部）、油化シェルエポキシ社製、エピコート１５２を１．５ｋｇ（１５重量部）、電気化学工業社製、デンカホルマール（登録商標）＃２０を０．８ｋｇ（８重量部）とジクロロフェニルジメチルウレア０．５ｋｇ（５重量部）を混合し、３０分間撹拌して樹脂組成物とし、これをシリコーンを塗布した離型紙にコーティングして樹脂フィルムとする。

【００７４】次いで、表面温度が６０～７０℃になるよう加熱した、周囲約２．７ｍの鋼製円形ドラムに、上記

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樹脂フィルムを巻き付け、次にクリールスタンドから巻き出した炭素繊維を、トラバースを介して上記円形ドラムで巻き取りながら該樹脂フィルム上に配列せしめ、さらにその上から前記樹脂フィルムで再度被覆した後、加圧ロールで回転加圧して樹脂を繊維束の内部に含浸せしめ、ドラムの回転数とトラバースの送り速度を適宜変更しながら、繊維目付が約２００ｇ／ｍ²、樹脂量が約３５重量％のプリプレグを作製する。このプリプレグを繊維方向が同一になるよう積層後、約２．９×１０⁵Ｐａの加圧下、１３５℃、２時間硬化せしめて巾２００ｍｍ、長さ２５０ｍｍ、厚み２ｍｍの複合材料片を得る。この材料片から、巾１２．７ｍｍ、長さは厚みの７倍としたものを試験片として切り出し、これを通常の３点曲げ試験治具を用い、支持スパンを試験片肉厚の４倍、歪速度を１．２７ｍｍ／分とした条件下で、破断荷重を測定する。このｎ＝８の平均値を破断荷重値とし、次式により求める。

ILSS（MPa）＝０．７５×（破断荷重値）／｛（試験片厚み）×（試験片幅）｝

【００７５】＜０゜引張強度＞ＡＳＴＭのＤ３０３９－７６に従って測定する。ＩＬＳＳの測定法と同様にしてプリプレグを作製する。このプリプレグを繊維方向が同一になるよう積層後、約２．９×１０⁵Ｐａの加圧下、１３５℃、２時間硬化せしめて巾２００ｍｍ、長さ２５０ｍｍ、厚み１ｍｍの複合材料片を得る。ゲージ長を１２７ｍｍとしてその両側に長さ約５０ｍｍのガラス繊維複合材料からなる厚み約１ｍｍのタブを貼り付け、この材料片から、巾１２．７ｍｍ、長さ２３０ｍｍの試験片を切り出し、これを通常の引張試験治具を用い、歪速度２ｍｍ／分で、破断荷重を測定する。また、繊維体積分率Ｖｆを６０％とし、得られた値より次式により０゜引張強度を求める。

０゜引張強度＝（破断荷重）×６０／｛（試験片厚み）×（試験片幅）×（繊維体積分率Ｖｆ）｝

ここで、破断荷重は、６個の試験片について測定した平均値であり、繊維体積分率Ｖｆ（％）は次式より求まるものである。

繊維体積分率Ｖｆ（％）＝１０×Ｙ×ｐ×ｎ／（ｄ×ｔ）
ここで、
Ｙ：炭素繊維目付（ｇ／ｍ）
ｐ：プリプレグ作成時の炭素繊維本数密度（本／ｃｍ）
ｎ：試験片作成時のプリプレグ積層数
ｄ：炭素繊維密度（ｇ／ｃｍ³）
ｔ：試験片厚さ（ｍｍ）
【００７６】＜表面から５０ｎｍの深さ部におけるＳｉとＣとの原子数比（Ｓｉ／Ｃ）＞ＳＩＭＳにより測定する。測定する炭素繊維を整列させ、真空環境下、下記測定装置、測定条件で、繊維の側面から一次イオンを照射し、発生する二次イオンを測定し、得られる炭素繊維の

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表面から５０ｎｍの深さ部における、ケイ素のカウント数と炭素のカウント数との比を（Ｓｉ／Ｃ）とする。
【００７７】・装置：ドイツ ATOMIKA 社製　A–DIDA3000
・一次イオン種：O²⁺
・一次イオンエネルギー：１２ｋｅＶ
・一次イオン電流：１００ｎＡ
・ラスター領域：２５０×２５０μｍ
・ゲート率：３０％
・分析領域：７５×７５μｍ
・検出二次イオン：正イオン
・電子スプレー条件：０．６ｋＶ－３．０Ａ（Ｆ７．５）
・測定時真空度：１×１０⁻⁶Ｐａ
・Ｈ－Ｑ－Ｈ：＃１４
【００７８】＜繊維表面におけるＳｉとＣとの原子数比（Ｓｉ／Ｃ）＞ＥＳＣＡにより測定する。測定する炭素繊維についてはサイジング剤が付着している場合は、次に示す前処理方法でサイジング剤を除去する。
【００７９】メタノールとクロロホルムの２：１（重量比）の混合液を用いてソックスレー抽出器で２時間環流後、１２時間、室温で硫酸に浸漬後、メタノールで充分洗浄、風乾する。続いて、下記測定装置、測定条件で、１００ｅＶ付近に観察されるＳｉ₂ₚのピークとＣ₁ₛピークとのピーク面積比を求め、次に示す装置の装置定数０．８１４を測定値に乗じて原子数比（Ｓｉ／Ｃ）とする。
【００８０】・装置：島津製作所製、ＥＳＣＡ７５０
・励起Ｘ線：ＭｇのＫα₁,₂線
・Ｃ₁ₛメインピークの結合エネルギー値：２８４．６ｅＶ
【００８１】＜フックドロップ長＞予め長さ約３ｃｍ、直径約０．５ｍｍのステンレス製針金を、円弧部の直径が５ｍｍになるように、フック状に折り曲げ、その一端に５ｇの重りをつけたものを用意する。
【００８２】測定するブリカーサーを約１ｍ採取し、一端を固定後、もう一端に単繊維本数１２０００本当たり５００ｇの重りをつけ、適当な場所で垂下する。
【００８３】前記フック部をブリカーサー上部の固定端から５ｃｍ下の糸束中心に差し入れ静かに放し、フック部が自重で鉛直方向に落下後、静止するまでズレ落ちた移動距離を測定する。少なくとも１０回の測定を行い、その相加平均値をフックドロップ長とする。
【００８４】＜油剤の加熱残存率ｒ＞測定する油剤試料を約１ｇ、直径が約６０ｍｍ、高さが約２０ｍｍのアルミ製の容器に採取し、オーブンで１０５℃、５時間乾燥する。得られた物質を空気中２４０℃で１２０分、次いで窒素中４５０℃で３０分、次に示す条件下で熱天秤（ＴＧ）により測定し、熱天秤におけるトータルの重量保持率を加熱残存率ｒとする。
・試料パン：アルミニウム製、直径５ｍｍ、高さ５ｍｍ

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・試料量：１５～２０ｍｇ
・空気中熱処理（手順１）
空気流量：３０ｍｌ／分
昇温速度：１０℃／分（範囲：室温～２４０℃）
熱処理時間（２４０℃）：１２０分
・雰囲気変更（手順２）
２４０℃のまま空気から窒素へ変更して５分間保持
・窒素中熱処理（手順３）
窒素流量：３０ｍｌ／分
昇温速度：１０℃／分（範囲：２４０～４５０℃）
熱処理時間（４５０℃）：３０分

【００８５】＜糸条の膨潤度＞乾燥緻密化前の膨潤糸約
１０ｇを測定試料とする。延伸脱水機を用いて、３０
００ｒｐｍで１５分間、表面付着水分を強制除去した後の
重量ｗ（ｇ）と、さらにこれを１１０℃で２時間熱風乾
燥機で乾燥した後の重量ｗ。（ｇ）から、次式により糸
条の膨潤度を求める。
糸条の膨潤度（％）＝（ｗ−ｗ。）×１００／ｗ。

【００８６】＜耐炎化糸のギ酸溶解度＞測定する耐炎化
糸約２．５ｇを熱風オーブンなどで１２０℃、２時間乾
燥した後、乾燥後の重量を精秤し、Ｇｐ（ｇ）とする。
２００ｃｃのビーカーに乾燥後の試料を入れ、純度９０
～１００％のギ酸を１００ｃｃ注ぎ、そのまま２５℃で
１００分間、振盪し処理する。この後、試料を取り出
し、流水中で６０分間、次に９０℃の温水中で２時間洗
浄する。さらに、１２０℃で２時間乾燥した後、乾燥後
の重量を精秤し、Ｇ１（ｇ）とする。得られた値より、
次式によりギ酸溶解度（％）を求める。
ギ酸溶解度（％）＝｛（Ｇｐ−Ｇ１）／Ｇｐ｝×１００

【００８７】＜重合体の［η］＞測定するアクリル系重
合体の乾燥試料７５ｍｇを２５ｍｌのメスフラスコに入
れ、０．１Ｎチオシアン酸ソーダージメチルホルムアミ
ド溶液を標線まで加えて完全に溶解した後、オストワル
ド粘度計を用いて２５℃で比粘度η。。を測定する。比粘
度η。。から、次式により［η］を求める。
$$[η] = \{(1+1.32η。。)^{1/2}-1\}/0.198$$

【００８８】＜耐炎化糸の炎収縮保持率＞測定する耐炎
化糸を約４０ｃｍ採取し、試長２０ｃｍとなるようにク
リップなどの不燃物で２点マークを付する。次に、一端
を固定し、もう一端から３０００ｄ当たり１０ｇの張力
を架け、糸条をブンゼンバーナー炎で加熱する。この
際、ブンゼンバーナーへの空気供給を調節し還元性の黄
色い炎を発生させ、マーク間を約１５秒／２０ｃｍの速
さで１往復半移動させ加熱する。加熱後のマーク間の糸
条の長さをＷｂ（ｍｍ）とし、次式により炎収縮保持率
（％）を求める。
炎収縮保持率（％）＝（Ｗｂ／２００）×１００

【００８９】＜炭素繊維の拡がり性指数＞単繊維本数が
３０００本以上の炭素繊維束を試料とし、単繊維本数１

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２０００本当たり１０００ｇｆの張力でクリールスタン
ドより巻き出し、油化シェルエポキシ社製、エピコート
（登録商標）８２８を含浸せしめた後、離型紙で表面を
覆った直径７３０ｍｍ、幅５００ｍｍの回転可能な鋼製
円形ドラムに一定速度でトラバースさせながら巻き取
る。ドラムを数回転させた後、巻き取り状態での糸幅を
０．１ｍｍ単位で測定し、ｎ＝３０の相加平均値をＷ
（ｍｍ）とし、試料である炭素繊維１ｍ当たりの重量を
Ｇｍ（ｇ）として拡がり性指数を次式により求める。
拡がり性指数＝Ｗ／Ｇｍ

【００９０】
【実施例】以下、実施例により本発明をさらに具体的に
説明する。製糸条件、焼成条件及びブリカーサーに関す
る主なデーターを表１に、炭素繊維、及び複合材料に関
する主なデーターを表２にそれぞれ示す。

【００９１】（実施例１）ジメチルスルホキシドを溶媒
とする溶液重合法により、アクリロニトリル（ＡＮ）９
７．６重量％とイタコン酸２．４重量％とからなる、
［η］が１．７、重合体の濃度が２２重量％の紡糸原液
を得た。重合後、アンモニアガスをｐＨが８．５になる
まで吹き込み、イタコン酸を中和して、アンモニウム基
をポリマーに導入することにより、紡糸原液の親水性を
向上させた。得られた紡糸原液を７０℃として、湿式紡
糸法により、直径０．０６５ｍｍ、孔数６０００の紡糸
口金を用いて、直接７０℃に温調した６０重量％ジメチ
ルスルホキシドの水溶液からなる凝固浴に紡出して凝固
させた。

【００９２】次に、凝固糸を７５、８５、９５℃の温水
中でトータルの延伸倍率が２倍になるよう延伸した後、
５０℃で水洗した。この浴延伸糸の膨潤度は２００％で
あった。

【００９３】次いで、浴延伸糸に、アミノ変性シリコー
ン、エポキシ変性シリコーン、及びエチレンオキサイド
変性シリコーンの混合物からなるシリコーン系油剤を付
与した。アミノ変性シリコーン、エポキシ変性シリコー
ン、及びエチレンオキサイド変性シリコーンの２５℃に
おける粘度は、それぞれ、４０００ｃＳｔ、１２０００
ｃＳｔ、及び５００ｃＳｔとし、混合比率は１０：１
０：１（重量比）である。ここで油剤の加熱残存率ｒは
４２％であった。

【００９４】さらに、１８０℃に温調した加熱ローラー
により乾燥緻密化を行った。

【００９５】乾燥緻密化の後、３ｋｇ／ｃｍ²−Ｇの加
圧スチーム中で、さらに延伸することにより、全延伸倍
率を１３倍とした。その後、糸条を３本合糸し、１ｋｇ
／ｃｍ²−Ｇの加圧空気で交絡処理を行って単糸繊度
０．８ｄ（ｄ：デニール）、単繊維本数１８０００本の
ブリカーサーを得た。このブリカーサーのΔＬ（明度
差）は２６であった。

【００９６】得られた繊維束を無撚状態のまま、２４０

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〜２８０℃の空気中、延伸倍率１．０倍で加熱して、炎収縮保持率７８％、ギ酸溶解度１．１％の耐炎化繊維に転換した。さらに耐炎化繊維を３００〜９００℃の不活性雰囲気中で延伸倍率１．０４で予備炭化後、最高温度１５００℃で炭化した。

【００９７】この後、重炭酸アンモニウムの水溶液中で、２０クーロン／ｇ−ＣＦの電解酸化処理を行い、炭素繊維を得た。得られた炭素繊維の品位は非常に良好であり、高い性能を示した。

【００９８】（実施例２）１ｋｇ／ｃ㎡−Ｇの加圧空気で交絡処理を行わなかったこと以外は実施例１と同様にして炭素繊維を得た。焼成工程において毛羽は多かったが、得られた炭素繊維の性能は良好であった。

【００９９】（実施例３）耐炎化、予備炭化の延伸倍率をそれぞれ０．９５、１．０とし、炭化における最高温度を１７００℃とした以外は実施例１と同様にして炭素繊維を得た。得られた炭素繊維の品位は非常に良好であり、高い性能を示した。

【０１００】（比較例１）温水浴での延伸倍率を５倍とした以外は、実施例１と同様にして炭素繊維を得た。なお、本例では浴延伸糸の膨潤度は２６０％まで上昇した。得られた炭素繊維の性能はやや劣るものであった。

【０１０１】（比較例２）１ｋｇ／ｃ㎡−Ｇの加圧空気で交絡処理を行わなかったこと以外は比較例１と同様にして炭素繊維を得た。焼成工程において毛羽が発生し、製造を途中で中断した。

【０１０２】（比較例３）耐炎化、予備炭化の延伸倍率をそれぞれ０．９５、１．０とし、炭化における最高温度を１７００℃とした以外は実施例１と同様にして炭素繊維を得た。得られた炭素繊維の性能はやや劣るものであった。

【０１０３】（比較例４）ジメチルスルホキシドを溶媒とする溶液重合法により、アクリロニトリル（ＡＮ）９８．８重量％とイタコン酸１．２重量％とからなる、［η］が１．７、重合体の濃度が２２重量％の紡糸原液を得た。重合後、アンモニアガスをｐＨが８．５になるまで吹き込み、イタコン酸を中和して、アンモニウム基をポリマーに導入することにより、紡糸原液の親水性を向上させた。得られた紡糸原液を７０℃として、乾湿式紡糸法により、直径０．１５ｍｍ、孔数６０００の紡糸口金を用いて、一旦空中へ吐出し、１０℃に温調した４０％ジメチルスルホキシドの水溶液からなる凝固浴に紡出して凝固させた。

【０１０４】得られた凝固糸を水洗した後、７０、８０、９０℃の温水中でトータルの延伸倍率が４倍になるよう延伸した。この浴延伸糸の膨潤度は８０％であった。

【０１０５】次いで、浴延伸糸に、アミノ変性シリコーン、エポキシ変性シリコーン、及びエチレンオキサイド変性シリコーンの混合物からなるシリコーン油剤を付与

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した。アミノ変性シリコーン、エポキシ変性シリコーン、及びエチレンオキサイド変性シリコーンの２５℃における粘度は、それぞれ、４０００ｃＳｔ、１２０００ｃＳｔ、及び５００ｃＳｔとし、混合比は１０：１０：１（重量比）である。ここで、油剤の加熱残存率ｒは４２％であった。

【０１０６】さらに、１８０℃に温調した加熱ローラーにより乾燥緻密化を行った。

【０１０７】乾燥緻密化の後、３ｋｇ／ｃ㎡−Ｇの加圧スチーム中で、さらに延伸することにより、全延伸倍率を１３倍とした。その後、糸条を３本合糸し、単糸繊度０．８ｄ、単繊維本数１８０００本のプリカーサーを得た。

【０１０８】さらに、比較例１と同様の焼成工程を経て、炭素繊維を得た。得られた炭素繊維の性能はやや劣るものであった。

【０１０９】（実施例４）ジメチルスルホキシドを溶媒とする溶液重合法により、アクリロニトリル（ＡＮ）９４．９重量％、イタコン酸１．２重量％とイソブチルメタクリレート３．９重量％とからなる、［η］が１．８、重合体の濃度が１８重量％の紡糸原液を得た。重合後、アンモニアガスをｐＨが８．５になるまで吹き込み、イタコン酸を中和して、アンモニウム基をポリマーに導入することにより、紡糸原液の親水性を向上させた。得られた紡糸原液を７０℃として、湿式紡糸法により、直径０．０７ｍｍ、孔数１２０００の紡糸口金を用いて、直接７０℃に温調した６０重量％ジメチルスルホキシドの水溶液からなる凝固浴に紡出して凝固させた。

【０１１０】次に、凝固糸を７５、８５、９５℃の温水中でトータルの延伸倍率が２倍になるよう延伸した後、５０℃で水洗した。この浴延伸糸の膨潤度は２０５％であった。

【０１１１】次いで、浴延伸糸に、アミノ変性シリコーンからなるシリコーン油剤を付与した。アミノ変性シリコーンの２５℃における粘度は４０００ｃＳｔとした。ここで、油剤の加熱残存率ｒは２５％であった。

【０１１２】さらに、１８０℃に温調した加熱ローラーにより乾燥緻密化を行った。

【０１１３】乾燥緻密化の後、３ｋｇ／ｃ㎡−Ｇの加圧スチーム中で、さらに延伸することにより、全延伸倍率を１３倍とした。その後、１．５ｋｇ／ｃ㎡−Ｇの加圧空気で交絡処理を行って単糸繊度１．１ｄ、単繊維本数１２０００本のプリカーサーを得た。

【０１１４】得られた繊維束を無撚状態のまま、２４０〜２８０℃の空気中、延伸倍率０．９５倍で加熱して、炎収縮保持率８５％、ギ酸溶解度１．５％の耐炎化繊維に転換した。さらに耐炎化繊維を３００〜９００℃の不活性雰囲気中で延伸倍率１．０倍で予備炭化後、最高温度１３００℃で炭化した。

【０１１５】この後、重炭酸アンモニウムの水溶液中

で、１０クーロン／ｇ－ＣＦの電解酸化処理を行い、炭素繊維を得た。得られた炭素繊維の品位は非常に良好であり、高い性能を示した。

【０１１６】（実施例５）重合体に、アクリロニトリル（ＡＮ）９８．８重量％とイタコン酸１．２重量％からなる共重合体を用いたこと以外は、実施例４と同様にして炭素繊維を得た。得られた炭素繊維の品位は非常に良好であり、高い性能を示した。

【０１１７】（実施例６）耐炎化、予備炭化の延伸倍率をそれぞれ０．９０、０．９５としたこと以外は実施例４と同様にして炭素繊維を得た。得られた炭素繊維の品位は非常に良好であり、高い性能を示した。

【０１１８】（比較例５）温水浴での延伸倍率を５倍とした以外は、実施例４と同様にして炭素繊維を得た。得られた炭素繊維の性能はやや劣るものであった。

【０１１９】（比較例６）耐炎化、予備炭化の延伸倍率をそれぞれ０．９０、０．９５としたこと以外は実施例５と同様にして炭素繊維を得た。得られた炭素繊維の性能はやや劣るものであった。

【０１２０】（比較例７）ジメチルスルホキシドを溶媒とする溶液重合法により、アクリロニトリル（ＡＮ）９８．８重量％とイタコン酸１．２重量％とからなる、［η］が１．７、重合体の濃度が２２重量％の紡糸原液を得た。重合後、アンモニアガスをｐＨが８．５になるまで吹き込み、イタコン酸を中和して、アンモニウム基をポリマーに導入することにより、紡糸原液の親水性を向上させた。得られた紡糸原液を７０℃として、乾湿式紡糸法により、直径０．１５ｍｍ、孔数６０００の紡糸口金を用いて、一旦空気中へ吐出し、１０℃に温調した４０％ジメチルスルホキシドの水溶液からなる凝固浴に紡出して凝固させた。

【０１２１】次に、凝固糸を水洗した後、７０、８０、９０℃の温水中でトータルの延伸倍率が４倍になるよう延伸した。この浴延伸糸の膨潤度は８０％であった。

【０１２２】次いで、浴延伸糸に、アミノ変性シリコーン、エポキシ変性シリコーン、及びエチレンオキサイド変性シリコーンの混合物からなるシリコーン油剤を付与した。アミノ変性シリコーン、エポキシ変性シリコーン、及びエチレンオキサイド変性シリコーンの２５℃における粘度は、それぞれ、４０００ｃＳｔ、１２０００ｃＳｔ、及び５００ｃＳｔとし、混合比率は１０：１０：１（重量比）である。ここで、油剤の加熱残存率ｒは４２％であった。

【０１２３】さらに、１８０℃に温調した加熱ローラーにより乾燥緻密化を行った。

【０１２４】乾燥緻密化の後、４ｋｇ／ｃｍ²－Ｇの加圧スチーム中で、さらに延伸することにより、全延伸倍率を１３倍とした。その後、糸条を２本合糸し、単糸繊度１．１ｄ、単繊維本数１２０００本のブリカーサーを得た。

【０１２５】さらに、比較例６と同様の焼成工程を経て、炭素繊維を得た。得られた炭素繊維の性能はやや劣るものであった。

【０１２６】（比較例８）重合体に、アクリロニトリル（ＡＮ）９４．９重量、イタコン酸１．２重量％とイソブチルメタクリレート３．９重量％とからなる共重合体を用いたこと以外は、比較例７と同様にして炭素繊維を得た。得られた炭素繊維の性能はやや劣るものであった。

【０１２７】
【表１】

表１

	浴延伸倍率（倍）	単糸繊度（ｄ）	フィラメント数	フックドロップ長（ｃｍ）	耐炎化延伸比	予備溶解度（％）	予備炭化延伸比	炭化温度（℃）
実施例１	2.0	0.8	18000	10	1.00	1.1	1.04	1500
実施例２	2.0	0.8	18000	10	1.00	1.2	1.04	1500
実施例３	2.0	0.8	18000	10	0.95	0.9	1.00	1700
比較例１	5.0	0.8	18000	8	1.00	1.0	1.04	1500
比較例２	5.0	0.8	18000	10	1.00	-	-	-
比較例３	5.0	0.8	18000	8	0.95	0.8	1.00	1700
比較例４	4.0	0.8	18000	10	1.00	1.5	1.04	1500
実施例４	2.0	1.1	12000	12	0.95	1.5	1.00	1300
実施例５	2.0	1.1	12000	12	0.95	2.5	1.00	1300
実施例６	2.0	1.1	12000	12	0.90	1.4	0.85	1300
比較例５	5.0	1.1	12000	10	0.95	1.4	1.00	1300
比較例６	5.0	1.1	12000	10	0.90	1.3	0.95	1300

【表２】

表2

	引張強度 (GPa)	弾性率 (GPa)	表面積比	三次元粗さ 二乗平均Rq (nm)	拡がり性指数	0° 引張強度 (GPa)	ILSS (MPa)	SI／C (50nm深さ)	SI／C (ESCA)
実施例1	6.3	296	1.05	17	24	2.2	97	0.2	0.008
実施例2	6.1	294	1.05	18	25	2.0	97	0.2	0.008
実施例3	6.0	293	1.04	18	30	2.0	93	0.1	0.000
比較例1	5.4	294	1.10	30	24	2.8	99	1.1	0.008
比較例2	－	－	－	－	－	－	－	－	－
比較例3	5.2	295	1.10	28	29	2.8	93	0.6	0.000
比較例4	6.3	296	1.00	8	24	2.2	83	0.1	0.010
実施例4	5.8	244	1.07	22	21	2.0	99	0.4	0.009
実施例5	5.5	238	1.06	21	22	2.8	99	0.4	0.008
実施例6	5.5	230	1.07	20	23	2.8	99	0.4	0.009
比較例5	4.5	240	1.12	31	21	2.2	100	1.0	0.011
比較例8	4.2	222	1.13	30	24	2.1	99	1.0	0.012

【０１２８】
【発明の効果】本発明の炭素繊維により、従来になく、軽量、高性能、かつコストパフォーマンスに優れる炭素繊維強化複合材料が得られる。かかる複合材料は、フライホイールのローター、ＣＮＧタンクなどのエネルギー＊

＊関連用途、航空機の一次構造材などに好適に使用することができる。
【０１２９】本発明のプリカーサーの製造方法により、強度と樹脂接着性の特性を両立した高い性能を有する炭素繊維を、安価かつ容易に得ることができる。